A RATIONAL FRAMEWORK FOR EVALUATING POTENTIAL ADVANTAGES AND POSSIBLE OBSTACLES TO PROCESS SIMPLIFICATION

by

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Abstract

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Considerable emphasis is given today to reduce the cost of chemical plants by simplifying their design. One way is to reduce the number of units by combining two or more steps into a single vessel. Although there were a few spectacular successes, large amounts of money have been spent on unsuccessful applications. In this thesis, an attempt is made to provide a systematic framework and quantitative criteria to evaluate the chance of success before large expenditures are made. Our method focuses on several criteria. 1: Does the combination of two steps into one unit create a synergism that improves both of them? If so, how strong is the synergism? 2: Are there any detrimental interaction due to this combination? 3: Do the two processes to be integrated share any dominant variables (state variables that strongly impact on process performance)? If so, is there a range of values, for these variables, acceptable for both processes?

For the majority of processes, examination of criteria 2 and 3 shows penalties, arising from the integration, that overweigh the advantages. It is often difficult to modify one of the processes; e.g. while membrane reactors are inherently attractive, it is hard to find membranes effective under reaction conditions.

Although the results have general applications, the thesis focuses on reactive distillation, a subject that achieved wide academic and industrial interest, but has had few large-scale implementations. We show that reactive distillation has large potential for processes involving azeotropes, as it allows implementation of counter-current reaction with miscible reactants in a single column. One of the main problems is that the temperature required for distillation is not suited for the reaction, due to either thermodynamic constraints or lack of catalysts. A main achievement of the thesis is the development of a new design concept, a non-reactive distillation column with several external reactors cascaded into it, able to retain the advantages of reactive distillation without suffering from its limitations. Finally, we show, using isomerization, that combining reaction and distillation, unlike a membrane, does not necessarily shift reaction conversion beyond equilibrium, but this depends on the specific reactive system.

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1. Introduction

Both the chemical and the refining process industries are more and more involved in finding ways of reducing the high capital cost incurred by the plants. There are several ways to achieve this cost reduction, but in this thesis we focused on an area that has recently received large attention in the literature, called process intensification, or process simplification as we renamed it (a definition of this concept is given in Chapter 2).

In complex multi-step processes, the investment cost reduction can be done in two ways: one of them is to change either the design or the chemical route of the process; the other is to combine two or more steps together into one unit. In the chemical industry, large sums have been spent on trying to achieve this goal, with relatively few successes compared to the large effort made. The goal of this thesis is to present a systematic methodology on how to evaluate new ideas for process simplification as well as its applicability and the chance of success. We will show that the application of this method could have saved large amounts of money in those developments that failed, as our methodology shows that these failures could have been recognized at an early research stage.

The methodology presented here integrates two previous methods developed by Prof. Shinnar and coworkers. The first method is differential economic evaluation of new processes[1-2], which analyzes new processes by comparing the differences between new and conventional processes. This method quantitatively evaluates the advantage that these differences give, focusing on the way the two processes deal with the constraints, kinetics, material of construction, etc..

The second methodology used in the thesis, which was realized by Prof. Shinnar and Prof. Rinard and their research group, is a recent development for the design and scale-up of new processes, called concurrent design[3-10]. This methodology focuses on determining and analyzing the dominant variables of a process, which are either internal flows or state variables that have a strong impact on process outputs and performance. Safe scale-up and good controllability require that all the dominant variables have to be independently controllable over a sufficiently wide range.

The thesis will focus on one important area of such process simplification, which is reactive distillation, a technology in which reaction and distillation are combined in one unit. This area led initially to a few successes[11-13], but since then has failed to lead to a large number of full-scale applications. It will be shown, in a simple and systematic way, how to select successful applications. The methodology of this work can be applied to a wide range of problems involving similar difficulties.

Both the separation unit and the reactor have dominant variables, such as temperature, space velocity, key component concentration, pressure, etc., that have to be kept within specific value ranges to meet specifications. When combining these two steps together it may happen that conflicts arise between the optimum ranges of values required by the dominant variables of the reaction and the separation. If the values of these dominant variables do not overlap over a sufficiently wide range, a compromise would be either costly or not feasible.

A typical problem faced in reactive distillation is that the temperature range required for the reaction does not overlap sufficiently with the range of temperatures needed for sufficient separation. In our terminology, the temperature is a dominant variable, and most of the time its desirable value is different for the two unit operations to be integrated. Thus, we have developed a criterion for deciding if such integration is feasible and advantageous. We have to evaluate the dominant variables of each process separately, estimate their permitted values and look at the overlap. We will later show that the lack of a sufficiently large common operative range of temperatures, as well as any other dominant variables, is the main reason why so few reactive distillation processes make it from laboratory to full-scale implementation.

A similar problem is encountered in membrane reactors, though for the membrane reactors there is a much higher potential to change the membrane properties, as, unlike distillation, it is not constrained by the thermodynamic properties of the compounds to be reacted and separated. Therefore, identification and analysis of the dominant variables are central for our methodology.

There is, however, another element of the integration. Integrating separation and reaction can lead to synergisms that completely change the process. For example, when we use a membrane reactor for a reversible reaction, the membrane physically removes the desired product from the reaction region. This removal can actually shift the reaction conversion further than the reaction equilibrium alone would allow at the same operative conditions. In reactive distillation one could expect a similar synergism, that is: the preferential removal of the product performs the same action as a membrane enhancing the total conversion obtained. But in a reactive column, in which the separation is achieved in several stages, the product stays in the unit until it is removed either from the top or the bottom. Therefore, a reactive distillation column does not act exactly like a membrane, but can only simulate it to an extent that depends on the specific process we are dealing with. Understanding this is especially important for binary reversible reactions or for multi-component reversible reactions with only one product, when the relative volatility is close to 1 (many trays are needed to remove the product from the reactive phase) and the reaction rate is low (large amounts of catalyst are required to achieve acceptable reaction conversions). In fact, in these systems, since the separation is not very efficient, the desired product is not quickly vaporized and it stays in the liquid (reactive) phase of the catalytic region, limiting the ability of the column to overcome the reaction equilibrium constraints.

For more complex reversible reactive systems, with two or more products (the desired product has to be either the lightest or the heaviest component in order to perform the reactive distillation in a single unit), the total conversion achieved in a reactive column can actually be larger than the reaction equilibrium. In this case, in order to achieve total reaction conversions larger than equilibrium, is sufficient that only one product is removed from the reactive phase. In fact, the equilibrium composition represents a limit only if all the products are present in the liquid phase, in sufficiently high concentrations, all at the same time.

A very strong synergistic effect that can be obtained in a reactive distillation column, for multiple feed reactive systems, is the ability to circumvent a reactant/product azeotrope by reacting away the compounds that form the azeotropes. On the other hand, a product/product azeotrope can be broken in a reactive column by extractive distillation. This works particularly well, as we will see in one of the examples studied, if one of the compounds already present in the unit also acts as an extractive agent. Actually, all successful examples of industrial implementation of reactive distillation involve azeotrope removal[12, 14, 15].

Combining a chemical reaction and a separation process is arguably the most promising field of process simplification and, among all the possible integrations between reaction and separation, reactive distillation is the technology whose implementation has been studied the most. Reactive distillation was first introduced and patented in the 1920's[16-19], while in the 1930's[20] the first article was published, but only a few decades ago it received new attention. Although many papers have been written[21-23] and patents filed about this technology, a simple and reliable methodology that helps one understand if a reactive system involving separation is a candidate for reactive distillation or not was never developed. The development of such a technique is therefore the purpose of this thesis.

There is a class of processes for which it is quite obvious that reactive distillation has an advantage, and it is easy to carry out the reaction inside the column. Regrettably, this only applies to a small class of reactions[11-13]. In other cases it is as much obvious that reactive distillation is not an option, as the penalties suffered would be larger than the advantages gained. In this thesis, which is divided into two separate sections prepared separately for publication (1 paper has been already published[24]), we will see examples of both successful implementations and applications that are not promising.

The first part of this work deals with the methyl-acetate production system, an example in which integration has a large synergistic effect. In this case the process replaced an older design with many separation steps (Figure 1), leading to a total change in process economics[13]. We will show that the reason for this success is that this process involves two azeotropes, one of which (methyl acetate/methanol) can be circumvented by completely reacting away one of the components (the methanol), while the other (methyl acetate/water) is broken by extractive distillation of water using as extractive agent the acetic acid, which is one of the reactants.

If one analyzes the problem as a reaction engineer, complete conversion in this reactive system requires the use of a counter-current reactor. But as the compounds are miscible, we need a counter-current train of reactors with distillation columns between each two reactors (Figure 2). The system can be simplified by bringing all the distillation columns together in order to form one tall column (Figure 3). This is as far as a designer can go in integrating the system if the reaction and the separation require different operative conditions. Luckily, from the analysis of the dominant variables of the two unit operations results that the reaction and the separation conditions match each other, allowing reaction and distillation to be carried out in one column (Figure 4).

Having understood this, we will show that one can achieve similar results, even if more expensively, by integrating all the distillation columns into one unit and keeping the reactors separated, as shown in Figure 3. This concept has the potential to be applied to many processes that involve difficult separations and equilibrium constrained reactions, although, precisely speaking, this is not reactive distillation since reaction and distillation are performed separately. However, one can still talk about process simplification as one has only 1 distillation column and 1-4 reactors (it depends on the complexity of the system) instead of a reactor plus eight non-reactive distillation columns, one liquid-liquid extraction column and a decanter, which were used in the previous process (Figure 1). Furthermore, other savings came from the elimination of all the required heat exchangers, control systems, pumps, and intermediate storage tanks.

The important point in this application of process simplification is that it shows how to circumvent the main obstacles faced when trying to apply reactive distillation technology to processes for which the operative conditions of the two unit operations do not match each other, namely:

1. the temperature required by the distillation is not suitable for the reaction, for thermodynamic and/or for kinetic reasons.
2. the catalyst cannot be easily loaded into the column because:
    a. the aging rate is too high.
    b. the catalyst activity is too low.

Other mismatches will be discussed in the thesis.

The second part, which is the 4th chapter of this work, deals with a simpler class of processes, reactions with an equilibrium constraint in which complete conversion can only be achieved by separating the unconverted feed from the desired product and recycling it back to the reactor.

There is a wide class of processes to which this applies, and many of them have been studied as potential cases for reactive distillation application and patents have been filed[25-27]. Here the cases faced are different from the case studied in ref. 24, for the following reasons:

1. in the examples belonging to the second part of the thesis, it is always possible to carry out the process in one reactor followed by one distillation column with recycle (Figure 5). Therefore, there is no intermediate case with a conventional distillation column with external reactors cascaded in it, and there is no way of simplifying the process while maintaining a separate reactor. In fact, a design similar to the one sketched in Figure 3, where outside reactors are cascaded in a distillation column, will complex the system, not simplify it.
2. the example from the first paper had one critical characteristic, which was the possibility of achieving a strong proper integration that led to a very large simplification. Furthermore, cost reduction overshadowed any increasing cost due to larger complexity in the design of the reactive distillation column[13].

   Intuitively there is a place to assume that the integration itself should lead to a large cost reduction and improved effectiveness of separation. A significant reduction in cost would allow us to attempt more complex simplification, with the possibility of suffering large penalties, as the advantages gained are also large, and still be ahead. But dramatic cost reductions and spectacular performance improvements do not happen in the examples belonging to this second class of processes analyzed. Therefore, as the simplification does not significantly impact the main cost of distillation, which is the reboiler heat duty (the reflux ratio is based on the total fresh feed flow rate), here the only possible reductions are the elimination of the reactor and the cost of the recycle. However, this reduction is balanced by the higher costs of reactive column internals.

Obviously, whenever the integration is easy to implement, it is a clear saving. However, in the majority of cases there is a penalty to pay. It will be clear that for these cases the maximum penalty that one can suffer has to be quite small to justify the higher costs of column internals, and time and money necessary for research and development of such a simplification.

At this point, we would like to remark that despite the fact that in this thesis the examples presented all deal with reactive distillation, the approach is presented in such a way that will allow this methodology to be applied to a large number of reactive systems followed by separation processes, non necessarily involving distillation, or any other integration of two separate unit operations in a single vessel.

The following chapter is dedicated to the introduction of our methodology, and to an exhaustive discussion about the general advantages and disadvantages of reactive distillation, when it is possible to apply it and what are the compromises when this technique is implemented. In the third and fourth chapter, our theoretical framework is applied to practical examples from the chemical industry. As already mentioned, the first example, the methyl acetate production system, is a process that shows such strong synergisms between reaction and separation to absolutely justify the use of reactive distillation. On the other hand, the examples in the fourth chapter deal with processes for which there is little room for process simplification, and reactive distillation does not always represent an attractive option.

For all the examples our conclusions were proved by performing computer simulations using Aspen Plus, a computer simulation program with many built-in thermodynamic laws, equilibrium equations, and provided with a large databank.

2. Theory

2.1 Process Simplification

The attempt to save both investment and operating costs, and possibly to achieve better performances, has brought about the development of “process intensification”. Researchers from both universities and industrial research centers have focused their effort more and more on trying to develop new techniques and realize novel devices that potentially could lead to higher performing and more economic processes. In the past two decades the interest in process intensification has truly emerged, becoming a major field of research in chemical engineering[16-19, 21-23].

Before discussing the details and goals of this work, and how we achieved them, we want to explain what is meant by process intensification and why we decided to rename it process simplification.

Through the years, several definitions have been given trying to clarify when an improvement or a new idea for a process falls in the category of process intensification and when it does not. Ramshaw, one of the pioneers in this field, opening the 1st International Conference on Process Intensification in the Chemical Industry (London 1995) defined process intensification as *“a strategy for making dramatic reduction in the size of a chemical plant so as to reach a given production objective”*[28]. The dramatic reduction that Ramshaw refers to can come from either smaller size of individual pieces of equipment or from employing a smaller number of unit operations. The main problem with this definition is that according to Ramshaw the volume reduction, to be significant, has to be at least of the order of 100 or more[28]. But in most cases such an intensification is not achievable, and a factor of two can be already considered a successful reduction.

Besides the factor of 100 for the volume reduction, it was also argued that describing the process intensification merely in terms of reduction of plant size and number of unit operations was too limiting for what the concept should include. The increment of production capacity within a device with a given volume, a reduction of the ratio between the energy consumption and the product obtained, and the cut in both wastes and by-product formation, were also considered as process intensification. On the other hand, process intensification should only concern engineering methodology and equipment development, hence the discovery of a new chemical route or the development of a better catalyst did not qualify as process intensification, no matter how dramatic the performance improvement could be. Therefore, a later definition stated that process intensification consists of *"the development of novel apparatuses and techniques that, compared to those commonly used today, are expected to bring dramatic improvements in manufacturing and processing, substantially decreasing equipment-size/production-capacity ratio* (but not necessarily employing a lower number of devices)*, energy consumption, or waste production, and ultimately resulting in cheaper, sustainable technologies."*[28].

Now, most of the tasks prescribed in the above definition are things that a skilled engineer would normally do while designing a new process, and it should not be indicated as a novel technique used in chemical engineering. Therefore, we came up with a new definition, different from the common idea of process intensification just given, and in order to avoid confusion we renamed it as "process simplification". In our definition *"process simplification consists of combining two or more unit operations into a single device, or in the discovery of a new catalyst or a new chemical route that* *drastically change the process. The new design can be developed either to improve the performances and lower the investment and operation costs of an existing process or it can represent the optimal solution for a new one"*. In example, the development of a new catalyst by Mobil in the Fischer-Tropsch process[29], discussed below, that simplified the whole plant and reduced the number of units employed, and therefore the costs, qualifies as process simplification.

In the past, research in this area has dealt mostly with the combination of reactors with one or more separation units. The driving forces, for attempting this kind of integration, have been:

1. the potential for obtaining productivity improvements and large economic savings. This can be achieved by increasing the overall rates, with a conversion of the reactants approaching 100%, which also benefits the reduction of recycle costs. Another productivity improvement can be reached by overcoming, when possible, very low reaction equilibrium constants, e.g., shifting the equilibrium by removing the desired product. Finally, a last contribution is the avoidance or elimination of difficult separation steps; in example, in reactive distillation, it is possible to avoid the azeotropes formation by completely reacting away one of the azeotrope component, this feature is particularly advantageous when the reaction produces a mixture of species that can form several azeotropes with each other.
2. the improvement in selectivity toward the desired products. In fact, removing one of the products from the reaction mixture or maintaining a low concentration of one of the reagents can lead to reducing of the rates of side reactions and hence improved

selectivity for the desired products. This also has as a consequence the reduction in the use of raw materials and the formation of undesirable by-products or waste.

3. the reduction of power consumption and a more efficient heat integration. For example we will look again at the reactive distillation systems. If the reaction is exothermic, the heat of reaction generated can be used to provide part of the heat required for the vaporization and, therefore, reduce the reboiler heat duty.
4. the reduction or the elimination of solvents and extractive agents. In the methyl acetate reactive system performed within a reactive distillation column, one of the reactants (acetic acid) also works as an extractive agent for removing water, which otherwise would form a low boiling azeotrope with the methyl acetate.

Some of these improvements are realized by using the reaction to improve the separation (e.g., overcoming azeotrope formation or reacting away contaminants); while other advantages are achieved by using the separation to improve the reaction (e.g., overcoming reaction equilibrium limitations, improving the reaction selectivity, or removing catalyst poisons). Naturally, the potential for major improvements is greatest when several aspects are important.

As a result of these possible integrations, new operations, coupling reaction and separation, have been realized. These include processes such as reactive distillation and membrane reactors.

In addition to coupling reaction and separation, another kind of simplification that has been studied is the integration of two separation tasks, with the development of the so-called hybrid separations[28]. In this case the non-economic goal is to couple the effects of two different separation techniques in a single vessel improving the overall separation efficiency when compared to the total efficiency reachable with the two units kept separated. For example, membrane distillation consists of bringing a volatile component of a liquid feed stream through a porous membrane as a vapor, and condensing it on the other side of the membrane into a permeate liquid. Membrane distillation allows a complete separation of the non-volatile components while reducing the risk of clogging the membrane pores.

2.2 Examples of Process Simplification

Let us explain the concept of process simplification in more detail by describing a few examples of both successful and failed applications.

One case, in which the change of the chemistry by a new catalyst led to a total change in the economics of the process, is the Fisher-Tropsch process. In this process, invented before World War II by I-G-FARBEN, coal is gasified producing syn-gas ($CO + H_2$), which is then reacted over a catalyst (composed by iron, cobalt and ruthenium) to form olefins $(CH_2)_n$. The process can produce gasoline, diesel, wax, and light gases, but one of its properties is that the molecular weight distribution is very wide. One can increase or decrease the molecular weight by changing the reaction temperature, but regardless of the catalyst the molecular weight distribution remains the same. This leads to large expenses as one needs complex refinery to separate the products and upgrade them into sellable products. The main cost item here is the refinery, but the source of this cost is the reactor, where the wide molecular weight distribution is produced. When Mobil, in the seventies, discovered a new class of catalysts, the so-called shape selective zeolites, it was found that these catalysts could convert in a single step, a low pressure hydro-treater, coal to high grade diesel, with a yield close to 95%. Mobil filed a patent[29] for a process in which the Fisher-Tropsch reactions shifted to as high molecular weight as feasible and converted the fractions boiling at 400 °F or more to high grade diesel in a single step. This reduced the investment costs by 1/3 and gave a much more valuable product by eliminating undesirable side-products.

A second very successful example, again invented by Mobil, was the disproportionation of toluene to xylene and benzene[30]. Here the desired products are benzene and p-xylene. The ortho and the meta xylenes, which were obtained in equilibrium distribution (because the disproportionation catalyst also catalyzes the isomerization), with only about 35% of the desired p-xylene, have to be separated and recycled to an isomerization reactor. The process was improved when a new shape selective catalyst was developed. This catalyst promotes the same reactions as the old one, but it has much more uniform and narrow pores, the size of which allows the toluene to enter and only the benzene and the p-xylene to escape. The active sites are inside the pores, the equilibrium reaction is exactly the same as it was with the old catalyst, but as the p-xylene is continuously removed, the isomerization is driven to completion. In that sense the catalyst particle is equivalent to a one-sided membrane reactor in which the feed enters through the pores, reacts on the active sites, and then the product exits through the same pores. Ref. 30 discusses how membrane reactors can effect both conversion and yield in complex reactions.

Next we want to show some unsuccessful examples of process simplification.

We chose here the methanol production from methane. One common process for producing methanol is by partial oxidation of methane, according to the reaction:

$$CH_4 + 1/2\ O_2 \rightarrow CH_3OH \qquad \Delta H_R^\circ = -\ 30.1\ \text{kcal/mole} \qquad \Delta G_R^\circ = -\ 26.6\ \text{kcal/mole} \qquad \text{(a)}$$

The name partial oxidation is misleading, as what really happens is combustion of methane with oxygen. The steam formed reacts, in the same reactor, with the remaining of methane to form syn-gas, which is close to equilibrium reaction:

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad \Delta H_R^\circ = +\ 49.3\ \text{kcal/mole} \qquad \Delta G_R^\circ = +\ 33.9\ \text{kcal/mole} \qquad \text{(b)}$$

The syn-gas formed is reacted, in a separate unit, to methanol:

$$CO + 2H_2 \rightarrow CH_3OH \qquad \Delta H_R^\circ = -21.6\ \text{kcal/mole} \qquad \Delta G_R^\circ = -\ 5.9\ \text{kcal/mole} \qquad \text{(c)}$$

The dominant cost factor is the oxygen separation unit.

An attempt of simplification was made by trying to carry out the overall reaction (a) in one reactor[31-32], which is feasible, but not attractive. The reason for that could have been seen in the experiments and there was no need for the large amount of money spent.

In the formation of methanol by partial oxidation in a single reactor, one faces one unsolvable problem. The methanol formed reacts with oxygen much faster, over any catalyst, than the methane does. Thus, one has to operate at low conversion, but will always combust methanol forming CO_2 + steam. This requires large amounts of oxygen. The best achieved selectivity of methane to methanol is 85%, with a 10% conversion per pass, as methanol is cheap it does not look so bad, but when we look at the oxygen, the selectivity is only about 60%. So, all we have to do is to compare the cost of the 40%

oxygen lost in the undesired side-reaction to the cost of the reactor saved; it turns out that the reactor, only 15% of the total plant cost, is cheaper.

However, in this example there is another factor that is typical of many process integrations: the reaction at low conversion requires a higher recycle. The methanol is easily separated by condensation, but the CO_2 is not easy to remove and will build-up in the stream of the recycled methane. The proposed process schemes all included a CO_2 separation from the methane recycle, which in itself made the process non economical. Although flow-sheets and cost estimates showed an advantage for the new process, this was never taken in consideration by any producers. This result could have been predicted from the exploratory experiments. What was neglected, in this development, was a proper estimate of the dominant cost factor and the realization that eliminating the reactor saves very little money, as this is not a dominant cost factor.

Another failed example, which is even more relevant with the topic of this thesis, is the development of a membrane reactor for the dehydrogenation of iso-butane to produce iso-butene[33]. The endothermic dehydrogenation reaction is equilibrium limited, and a suitable membrane would remove the equilibrium constraint. The main advantage of this integration is not the elimination of the recycle, but the ability to lower the operative temperature and still get reasonable conversion. This would drastically reduce the side reactions, such as the coking of the catalyst that depends on temperature, and simplify the design reducing the investment cost of the process. However, all the attempts to do so failed until now because presently hydrogen-selective membranes lose their selectivity at high temperature.

2.3 Definition of the Methodology and Goals of the Thesis

Once the idea of process simplification has been clarified, we can explain our methodology and discuss the main goals that we want to achieve in this thesis. Our intent is to build up a theoretical framework that can help a designer, at a very early stage of a process development, understand if the process that he or she is developing is suitable or not for process simplification. Currently in the literature there are only a few useful guidelines on how to decide whether or not reactive distillation is a good process concept[34], but no comprehensive set of general rules is known for deciding feasibility of process simplification.

Our methodology is, in general, a two-step task:

1. first, one has to study the process from a design engineer point of view, identifying all the constraints, limitations, and dominant variables of the process. Then, based on these conclusions, one has to realize a design that is able to meet the specifications keeping the dominant variables independently controllable, and overcome the limitations without violating the constraints. When a valid design has been obtained, one has to analyze the dominant variables in terms of the range of acceptable values that they can assume. Finally, one has to see if the simplification of the process is physically achievable by verifying that the integration does not cause any mismatch between the optimum ranges of values required for the dominant variables of the two units.
2. second, once a simplification has been proven to be feasible, one still needs to determine whether or not it is profitable. Therefore, one will balance the advantages

acquired and the disadvantages suffered, and decide if simplifying the process is convenient or not.

In this research we focused our attention mostly on reactive distillation because the interest that researchers have shown for the potential offered by this methodology has not been matched yet by any other type of process simplification. The extensive academic and industrial research in the area has resulted into a large number of both articles published and patents registered on the subject[21-23]. But, despite this effort, only few successful applications can be enumerated, such as MTBE, ETBE, and methyl acetate production systems[12, 14-15].

We will explain the reasons why reactive distillation technology only has so few implementations. We will see that this basically depends on the difficulty of matching the operating conditions required by the reaction with those required by the separation process. Another reason is that, unlike a membrane, a distillation column does not physically remove the desired product from the reactive systems as soon as it is formed, but it takes several stages to accomplish this. Therefore, depending on the process, the conditions within the reactive column could be such that the reaction equilibrium limitations are not overcame. We will come back to this later, in Chapter 5, once the examples studied have been discussed.

The last goal of this thesis is the development of a design concept that has a much larger potential than reactive distillation to be applied to all those processes that involves difficult separations and equilibrium constrained reactions, but for which the desired operative conditions for reaction and distillation do not match. This design is composed of a non-reactive distillation column connected to several external reactors (Figure 3). Although this design is not a reactive distillation column anymore, as reaction and distillation are performed in separate units, it allows us to remove all the constraints that limit the applicability of reactive distillation and still has most of the advantages that could be gained with reactive distillation.

While we use reactive distillation as an example, the results are of general validity.

2.4 Applicability of Reactive Distillation

In this section we will discuss when it is possible to implement reactive distillation, the advantages and the limitations of this technology, and the reasons why the number of successful applications is still so small. We will see that if we want to integrate two or more steps of a process into one unit, we face a general problem, that is: the two unit operations may require different dominant variables, and even when the dominant variables are the same, they may require different values.

The concept of dominant variable was first introduced by Professors Shinnar and Rinard, and co-workers during the development of a methodology for the concurrent design of complex chemical plants and their control systems. A dominant variable is defined as either a state variable or an internal flow, which has a strong impact on the outputs of the system and on its stability[7-9]. The value that a dominant variable can assume is not represented by a single point, but rather it lies within a range of acceptable values.

When performing a process simplification, it may happen that the two unit operations share a dominant variable (i.e. temperature is dominant for both reaction and separation), but the range of acceptable values of the dominant variable for the first unit does not overlap, or does not overlap sufficiently, the range of acceptable values of the same dominant variable for the second unit (i.e. reaction and separation require different values for the temperature). This difficulty of matching either the dominant variables or the different requirements for the same dominant variable makes, very often, the simplification not convenient or even achievable at all. On the other hand, it is clear that the simplification, whenever it is applicable, has its advantages, especially economics, as it can lead to strong synergistic effects.

Therefore, *conditio sine qua non* for integrating two unit operations in a single device is that the operative conditions of the two steps have to match each other.

In reactive distillation the dominant variables are: temperature, pressure, feed flow rate, feed composition, reflux ratio, catalyst activity, and space velocity. The most critical variable here is the temperature, as it is dominant for three different aspects: separation, reaction equilibrium (or thermodynamics), and kinetics.

The integration of separation and reaction requires, in general, the existence of a common range of acceptable temperatures that satisfies separation, thermodynamic, and kinetic requirements, and the matching of the space velocity with the requirements of the column (diameter and number of stages, which are fixed by the separation requirements and, therefore, depend on the reflux ratio, as it determines the column internal flow rate, once the feed flow rate is fixed). Furthermore, these matched ranges have to be as wide as possible in order to provide the design with the ability of maintaining product purities and reaction conversion at the desired level when there are disturbances in feed composition, change in product specifications and other variations. In fact, in a reactive distillation column, controllability of the process remains a main issue in assuring the feasibility of the desired split.

Next, we want to explain in detail why this matching is so difficult to achieve.

In distillation the temperature, which affects the separation coefficients, is determined by separation requirements, and it assumes values intermediate between the boiling points, at the operative pressure (which is a dominant variable for distillation), of the components present in the unit.

On the other hand, the conditions for the reaction are fixed by the equilibrium of the reaction and by the properties of available catalysts; in other words, the reaction temperature depends in turn on the matching between the optimum conditions for reaction equilibrium and for reaction rate.

In reactive distillation, the acceptable temperature range for separation and the acceptable temperature range for reaction (which comes from the matching of other two temperature ranges) have to match each other. Regrettably, this happens very seldom.

When the optimum conditions for the temperature do not match, it is generally the reaction that requires temperatures higher than the distillation, but higher separation temperatures can only be achieved by changing the pressure in the column. Unfortunately, in many separation processes, the pressure (which is also constrained by hot and cold utilities), and therefore the temperature, can only be varied over a narrow range, since increasing the pressure will change or even reverse the relative volatility. This is the case of the methyl acetate production system[24]. At high pressure (Table 1) the boiling point of methanol (one of the reactants) becomes lower than the boiling point of methyl acetate (the desired product), which cannot be separated any more from the top.

In distillation, reflux ratio is used as a manipulated variable to meet the process specifications, but a manipulated variable can also be a dominant variable[9], and this is the case of the reflux ratio, which is dominant for separation. Furthermore, the reflux ratio also determines the flow rates internal to the column, which in turn define other important parameters of the distillation column. In fact, the down-flowing liquid and up-flowing vapor streams give the size of the column, and therefore the maximum amount of catalyst that can fit inside the column, which defines the reaction volume. Lastly, the reflux ratio, by fixing the necessary vapor flow rate, also determines the most important parameter for economics evaluation in a distillation column, the heat to be provided to the reboiler in order to achieve the desired product purity.

For the space velocity, the dominance depends on the physical state of the catalyst. When the catalyst is heterogeneous, the space velocity cannot be manipulated independently since the size of the column is determined by the separation requirements, and not by the reaction. Therefore, in this case, the space velocity is only dominant at the design stage, when the reaction volume is fixed and the quantity of catalyst that can be provided is also determined. The available catalyst has to have a high activity over the overlapped temperature range and very low deactivation and aging rates, otherwise it would be needed a very large and tall reactive column (to fit in enough heterogeneous catalyst and have sufficiently long residence time) to be able to achieve the required reaction conversion, and it may be more economical to use a reactor + separator arrangement. On the contrary, when the catalyst is homogeneous, the space velocity can be freely adjusted by simply feeding to the reactive column more or less catalyst. Naturally, similar to the heterogeneous case, a very active catalyst would avoid a big reactive column (to provide long residence time) and feeding large quantity of homogeneous catalyst (which increases the costs of catalyst recovery) to meet the product specifications.

While in a reactor the pressure is only dominant when the reaction takes place in the gas phase and is not equi-molar, in distillation, of non-ideal systems, it is dominant, as it changes the relative volatility. However, pressure is not independent of temperature and, therefore, although dominant, it cannot be freely manipulated.

The feed flow rate is dominant, as it can change the process outputs. Its value, which determines the amount of total material processed in the system, depends on the productivity specifications.

Finally, the feed composition is also a dominant variable, as it can change the reaction conversion, therefore the column composition profile, and ultimately the desired outputs. This is particularly useful when we manipulate it in order to feed one of the reactants in excess to improve the conversion. However, since the value for the limiting reactant is imposed on the column by the market to guarantee the desirable productivity, the feed composition is manipulated accordingly with the feed flow rate.

In addition to the dominant variables, there are also some constraints that might limit the applicability of reactive distillation[35]. First, we have to make sure that there are no volatility constraints. This means that the reagents and products must have suitable volatility capable of maintaining high concentrations of reactants and low concentrations of products in the reaction zone.

If a homogeneous catalyst is used (generally the highest boiling component), the desired product has to be the lightest component, otherwise it would leave the column from the bottom with the catalyst and another separation step would be needed. On the other hand, when a heterogeneous catalyst is used, there are also constraints due to the catalyst regeneration and flow mal-distribution. In fact, the physical state of the catalyst itself is the cause of limitations that are not faced when the two unit operations are performed in separate vessels. With a solid catalyst the operations of catalyst regeneration and replacement are not possible on-line. Also, some standard ways of compensating for the catalysts deactivation, such as raising the temperature or frequent catalyst regeneration, are not feasible inside the distillation column. The only way to regenerate, or replace the solid catalyst, is by shutting-down and starting-up the unit, which would be highly time and money consuming. That is the reason why heterogeneous catalysts can be used in reactive distillation columns only when they have a very low deactivation rate. Furthermore, a solid packed in a column requires complex and expensive tray internal designs to reduce the impact of flow mal-distribution. In fact, in order to compensate for the deterioration of separation efficiency in the reactive section, more trays have to be built compared to the ideal case with 100% separation efficiency. The difficulties of flow mal-distribution are faced especially during the scale-up of the process, because liquid distribution in packed reactive distillation columns is particularly problematic when dealing with very large flow rates.

2.5 Cases for which the Application of the Reactive Distillation Technology Is Convenient

All the expenses and penalties faced in reactive distillation have to be weighted against the advantages gained with the simplification. The savings can be significant if the following are intrinsic in the process:

a. the desired temperature range for the reaction (which comes from the matching of the temperature ranges valid for thermodynamics and kinetics) overlaps the desired temperature range for the separation.
b. the catalyst utilized is either homogeneous and/or is very active with a very low deactivation rate.

Regrettably, there are very few examples in which these apply. However, if there is a strong synergism, as in the methyl acetate production system, then the expense to afford, in order to overcome these difficulties, is justified. There are several types of systems in which such a synergism would exist:

1. reactions with complex separation processes or involving azeotropes formation. This was observed in MTBE, ETBE, and methyl acetate production systems[11-13, 36].
2. reactive systems where the desired product is an intermediate.
3. reactions with equilibrium limitations.

In this thesis we focused on the first and the third case.

Processes that fall in the first type of reactive systems cannot be carried out in a simple scheme composed by a reactor and a distillation column, because the processes require complex separations, especially when azeotrope formation is involved. In these cases, when the operative conditions match, the integration can be very convenient. The methyl acetate production system is such a process[24]. Here, the complexity of the problem is not only due to a reaction with low equilibrium, but also to the formation of two minimum boiling azeotropes. In this process we have a quaternary reactive system in which methanol reacts with acetic acid to give methyl acetate, also forming water as a by-product, with sulfuric acid as a catalyst.

For the methyl acetate production systems, due to the complexities mentioned above, a simple scheme composed by a reactor plus a non-reactive distillation column, as sketched in Figure 6, does not work. In the next chapter we will show how, facing the problem from a reactor engineer point of view, is possible to derive a design (Figure 3) much cheaper and efficient than the older methyl acetate process (Figure 1). This design is obtained without integrating reaction and separation. Then, starting from the design in Figure 3 and analyzing the dominant variables, as prescribed in our method, we will see that it is possible to simplify the design in order to obtain the final reactive distillation column (Figure 4).

This example, and how we derived the final design shown in Figure 4, will be studied in more detail in the next chapter of this thesis.

However, for the methyl acetate production system all the pieces fall perfectly into place, and the advantages gained, especially economics, are far more than the disadvantages suffered. In fact, the implementation of the reactive distillation technology has reduced the investment and the operating costs by almost an order of magnitude by eliminating a whole series of complex separation processes[12, 13, 36] (Figure 1).

On the contrary, the systems that belong to the third category of processes can be performed in a reactor coupled with a non-reactive distillation column, with recycle of unconverted reactants back to the reactor (Figure 5). Therefore, we only have one reactor and one distillation column and all one can do is eliminate the reactor, which only pays if the conditions cited before match. In fact, if the same process is carried out, without penalties, in a reactive distillation column, this solution is always preferable. But, if there are penalties to pay, the simplification is convenient only when combining the two unit operations leads to significantly strong synergisms between reaction and separation. Hence, we have to evaluate if there are any potential synergisms when eliminating the reactor that can justify the costs of the simplification. For these types of systems, we will analyze the limitations and the advantages introduced by the implementation of the reactive distillation technology, when possible, in a given process. The balance between losses and gains due to the simplification determines whether or not to apply this technology. Examples of systems with reactions showing equilibrium limitations are presented in Chapter 4 of the present work.

Before concluding this chapter, it is important to mention a last disadvantage of process simplification, which concerns the controllability of a reactive distillation column. In the concurrent design theory mentioned before[9], the practical degrees of freedom of a process, for control purposes, are defined as the number of independently controllable dominant variable. And, if a dominant variable can be kept at ‘n’ different levels, each having an independent impact on the process, then that variable itself counts as ‘n’ practical degrees of freedom. Now, because of the implementation of reaction and separation in a single vessel, the temperature ranges for separation and reaction are not independent any longer for control purposes; therefore we lose a practical degree of freedom. Another practical degree of freedom, the space velocity, is lost if the catalyst is heterogeneous, as the reaction volume and the amount of catalyst filled in the column are fixed at the design stage and the space velocity cannot be freely manipulated.

Here, we do not refer to controllability in a conventional way (dynamic control), but we refer to feedback control. In other words, the loss of practical degrees of freedom affects the ability of the steady state control system to achieve the desired performance, which would allow the process to meet the specifications.

Most of the limitations discussed here, especially when a heterogeneous catalyst is used, can be overcame by designing a non-reactive distillation column with external reactors cascaded into it, like the design sketched in Figure 3. Using this design, the temperature can be independently fixed for the separation and the reaction, and we regain the practical degree of freedom lost with the process simplification. Also, continuous catalyst make-up, regeneration, and replacement are possible by shutting down one reactor at a time while operating the rest of them. Furthermore, we can fix the space velocity independently of separation constraints by building reactors as large as necessary in order to fit enough catalyst in it and provide the required residence time, and regain the other practical degree of freedom lost. Finally, the non-reactive distillation column does not have problems of flow mal-distribution, and hence has a better separation efficiency. The design in Figure 3 is important for those designs that would require reactive distillation but for which the operation conditions do not match. However, we can no longer talk about reactive distillation, and it is important to point out that outside reactors are not cheap, since they are not completely integrated, and therefore should only be used when there is a strong synergism.

3. Methyl Acetate Production System

3.1 Introduction

In this chapter we want to demonstrate our methodology by applying it to an actual example. We will use the methyl acetate process due to the large amount of data available for reliable simulations. The results will also allow us to explain what are the limitations in the current application of reactive distillation. Finally, we will show how, applying our methodology, can obtain a design able to retain most of the advantages that one would expect from reactive distillation, without suffering from the limitations and constraints of this technology.

3.2 Overview

As mentioned earlier, reactive distillation has been in practice for over twenty years, but has had only a few spectacular successes, such as the production of methyl acetate. The number of actual installations is quite small compared to the large number of patents, papers and extensive academic and industrial research in the area[14-15, 21-23, 37]. Here, we try to elucidate the reasons for that.

The main reason, as explained in the previous chapter, is that it is difficult to match the optimum conditions for distillation and reaction. In distillation, pressure is the only variable that can change the operative temperature range for the separation. Regrettably, many distillation processes are very inflexible in the conditions required as boiling points change with pressure and, therefore, the corresponding temperature has a narrow range. The conditions for reaction, on the other hand, are fixed by the thermodynamics and by the properties of available catalysts. In this sense, reactive distillation shows the general problem of process simplification: when carrying out two tasks in the same unit, it often involves compromises between reaction and separation conditions that negate the cost advantages gained by the simplification. Thus, for many interesting cases, the optimum temperature range for the reaction (that satisfies both thermodynamics and kinetics requirements) is usually different from that required for distillation. Also, low space velocities are difficult to achieve inside a distillation column and some standard ways of compensating for the deactivation of catalysts, such as raising the temperature or frequent catalyst regeneration (for heterogeneous catalyst), are not feasible inside the distillation column. Therefore, the only successful realizations are those to which the above limitations do not apply.

On the other hand, reactive distillation has potentially significant advantages for systems involving azeotropes or complex separations, which is the case of the example shown in this chapter. For example, it permits the design of counter-current reactors with two miscible reactants. Here, we thoroughly analyze design modifications that allow one to achieve the full advantages of reactive distillation while keeping distillation and reaction in separate vessels.

Reactive distillation for producing methyl acetate reduced investment and operative costs by almost an order of magnitude as it eliminated a whole series of separation processes[13]. Since the methyl acetate process has a very active homogeneous catalyst, it can easily be realized in a single reactive column. The cost reduction is far larger than could be expected with process simplification.

The reaction of methanol with acetic acid has constraints that cannot be overcome in the standard way of coupling the reactor with a distillation column (Figure 6) because of the methyl acetate-methanol and methyl acetate-water azeotropes. The existence of these two azeotropes requires a very complex separation process. The counter-current reactive distillation column eliminates the methyl acetate-methanol azeotrope by achieving complete conversion of methanol and breaks the methyl acetate-water one by extractive distillation. Furthermore, this design also permits a reaction extent much larger than equilibrium would permit. In fact, due to the evaporation occurring at each stage, methyl acetate (the lowest boiling component) is continuously removed from the liquid phase (phase in which the reaction occurs), moving the reaction equilibrium toward the formation of methyl acetate. In all the simulations performed for this example, we assumed that the reaction only takes place in the liquid phase.

We will show that similar advantages can be achieved by combining the non-reactive distillation column with four external reactors, but this is more expensive than a single reactive column. However, the new design (Figure 3) still retains the large economic advantages over the conventional process shown in Figure 1. This design could be successfully applied to a much wider set of complex processes than reactive distillation. The results presented provide a useful tool for those who want to investigate if reactive distillation is suitable for their processes or what potential advantages there could be.

To achieve this goal, we will first derive the external-reactor column by generating the design alternatives of the methyl acetate production system. This is done by analyzing the design and development of the process from a reaction-engineering point of view. Then, we will identify the dominant variables of this system by applying the concurrent design technique. Finally, we will compare the process performance between the reactive column and the distillation column with external reactors.

3.3 Technical Background

Since our methodology is strongly based on the concurrent design method, it is desired to give a brief explanation of this method and the definition of the key concepts. A detailed explanation on partial control and concurrent design methodology and how to implement them can be found in Shinnar et al. (2000)[7], while specific mathematical and thermodynamic formulations can be found in Kothare et al. (2000)[8] and Tyréus (1999a,b)[38-39].

In recent years, the research group headed by Professors Shinnar and Rinard has proposed a concurrent design technique based on partial control for complex chemical processes[3-9]. The main idea of the concurrent design is that even very complex systems can be safely built if the designs of both the process and its control structure are carried out simultaneously.

In complex chemical systems, the number of process variables to be controlled is usually larger than the number of available manipulated variables. The central premise of partial control is that if we control a subset of variables that greatly affect the performance of the process, we can maintain the other variables within their desired ranges. The variables in this subset are called dominant variables[5, 40]. This concurrent design methodology has already been successfully applied to fluidized catalytic cracker (FCC) and crystallizer modeling[8, 41].

The primary goal of a plant is to produce products within desired specifications. If we do not meet the specifications, the plant fails. There are two types of specifications, product specifications (i.e., conversion, purity, product properties, etc.), and process specifications (i.e., productivity, adaptability to different operating conditions, change of feed, etc.). In addition to the specifications a plant is also bounded by some process constraints, which generally regard catalyst properties, process kinetics, materials of construction, gas effluent concentration, hot and cold utilities availability, margin of action of manipulated variables, etc. The specifications must be met in the face of disturbance in production rate, feed composition and other connection to the environment. Independently controlling the dominant variables enables us to achieve plant operations within the desired product and process specifications.

The dominant variables are identified through a full understanding of the process. This identification can be done by using learning models such as literature, bench-scale or pilot plants experiments, and computer simulation models. Sensitivity analysis is very useful to determine dominant variables in computer simulations. Once these variables have been selected, it must be studied which of the dominant variable can be independently controlled. The number of the dominant variables that can be independently controlled determines the practical degrees of freedom[7-9]. Furthermore, if a dominant variable can assume different values, in different section of the process, each with an independent impact on the process, then each of these values define a practical degree of freedom. Having a large number of practical degrees of freedom is very important in terms of achieving stable steady state operation, and being able to meet the desired specifications.

The steps concerning the identification and the analysis of the dominant variables are essential, in our methodology, for determining the feasibility of process simplification.

3.4 The Methyl Acetate Production System

Under some circumstances, reaction and distillation can be integrated in a single operation unit. Such integration can result in dramatic economic effects in terms of process miniaturization and simplification. For example, one reactor and nine separation columns were involved in a conventional process to produce methyl acetate. But in the early eighties, Eastman Chemicals developed and built a single reactive distillation column that did the same tasks as the ten unit-operations[12, 36]. It was reported that the operating and investment costs were reduced to less than one-fifth the costs of the conventional process[13]. Since this process came out, both academia and industry have been actively involved in applying reactive distillation technology to other systems. Detailed reviews on reactive distillation can be found in Buzad and Doherty (1992)[42], Taylor and Krishna (2000)[22] and Malone and Doherty (2000)[23].

Methyl acetate (MA) is produced via esterification of acetic acid (AC) with methanol (MT). The reaction takes place in the presence of sulfuric acid (SA) as a catalyst and also forms water (W) as a byproduct:

$$CH_3COOH\ (AC) + CH_3OH\ (MT) \quad \overset{H_2SO_4\ (SA)}{\Leftrightarrow} \quad CH_3COOCH_3\ (MA) + H_2O\ (W)$$

$$\Delta H_R^\circ = -\ 4.8\ \text{kcal/mole}$$
$$\Delta G_R^\circ = -\ 3.8\ \text{kcal/mole}$$

Recovery of pure MA by distillation is very difficult due to the presence of two minimum boiling azeotropes. One azeotrope is MA-W (5 wt% of W at 1 atm) and the other is MA-MT (18 wt% of MT at 1 atm). Furthermore, a tangent pinch between AC and W makes the recovery of unconverted AC very expensive. Table 1 shows boiling points for pure components and azeotropes at two different pressures. AC is the highest boiler, while the MA-MT azeotrope is the lowest boiler.

3.4.1 Generating Design Alternatives

A conventional scheme for producing MA would be a reactor followed by a non-reactive distillation column as shown in Figure 6. An excess of one of the two reactants is needed to achieve high reaction conversion. However, no matter what excess of AC or MT is used, pure MA cannot be separated at the top of the column due to the formation of the two minimum boiling azeotropes (MA-MT and MA-W)[13]. Furthermore, unconverted acetic acid would be very hard to recover at the bottom because of the tangent pinch it forms with water.

The only way to improve the product purity to the values required by market demands is to circumvent the azeotropes. In this example, both the azeotropes can be overcome. Specifically, the product/reactant azeotrope, between MA and MT, is circumvented by reacting away MT, which results in a very high reaction conversion (over 99%). On the other hand, the product/product azeotrope, between MA and W, can be broken by extractive distillation. Luckily enough, one of the reactants, AC, also works as an agent for water extraction. A scheme that would be able to get rid of both azeotropes, while producing high purity MA, requires the use of several reactors connected to each other in a counter-current manner as shown in Figure 2. In common practice, counter-current schemes are usually used when the systems are immiscible as in L-L extraction processes. Since the methyl acetate system is miscible, we have to put separation units between the reactors. AC is fed to an extractive distillation column where it breaks the MA-W azeotrope, while MT is provided at the opposite end. In this way, the final conversion would be higher than it is in the single reactor of Figure 6 because the reaction takes place with a large excess of one of the two reactants in each reactor. Pure methyl acetate is the top product of the extractive distillation column while acetic acid excess leaves the process with by-product W and SA catalyst. The problem with this scheme is that it would be very expensive to recover excess AC from W.

What can be observed in Figure 2 is that all the columns and reactors are fed with the same components, but their concentrations change along the counter-current train. This feature suggests to us that all the columns can be put together, if they are not too tall, in order to form a single separation column as shown in Figure 3. From this single column it is possible to withdraw side streams into external reactors and to return the reacted streams back to the column in a manner similar to the counter-current scheme in Figure 2. The two reactants are still fed counter-currently in Figure 3 while the SA catalyst is only provided to the first side-reactor since it flows down with the liquid stream into the other reactors. This design, which is much cheaper than the original design shown in Figure 1, has been obtained without requiring any matching between the optimum operative conditions of reaction with those of distillation.

A further improvement in this design can be only achieved if the analysis of the dominant variables shows that the operative conditions for distillation and reaction match. In this case, the reactors can be incorporated inside the column and both tasks performed simultaneously (Figure 4).

In summary, we showed how, facing the problems from a reaction engineer point of view and applying our methodology, which strongly depends on the correct identification and analysis of the dominant variables, we could design the counter-current distillation column with external reactors in Figure 3. And then further simplify the design in order to obtain the reactive column used by Eastman Chemicals for the MA production in Figure 4, without performing any experiments or simulations.

Despite the fact that process simplification cannot be applied in general, but is only feasible when the operating conditions of the reaction and separation match each other (widely discussed in section 2.4), whenever applicable, there are several advantages of this process simplification. The most interesting one is that we can build a more compact plant using a smaller number of units, and consequently save installation and operating costs. Also, with this design it is possible to break both the azeotropes, and to achieve a reaction extent larger than equilibrium would permit. All these advantages can be translated into a total cost reduction as large as 80%[13].

3.4.2 Specifications and Constraints

As already mentioned, product specifications are the most important specifications since off-spec products cannot be sold in the market. Here, the main product specification is MA purity at the top and it is required to be at least 99 mole % (or 99.5 weight %)[12]. Hereafter, the MA purity is expressed as mole % throughout the chapter. This value can change according to different market demands. On the other hand, an important process specification is the production rate (productivity) of MA, or in other words, the distillate flow rate (D) to timely supply the required quantity of the product to the market. Similar to the product purity, the set-point of the distillate flow rate is also fixed by the market demand, and its set-point only changes when the feed flow rates, or their concentrations in terms of MT and AC feed flow rate ratio, change. For economic reasons the bottom by-product purity (methanol < 1%, and traces of methyl acetate) is also fixed.

The usage of SA causes a corrosion problem, specifically at the bottom where the temperature in the column is the highest. To minimize the corrosion problem, the bottom temperature has to be maintained as low as possible and/or more expensive materials can be used.

3.4.3 Identification of Dominant Variables

Dominant variables are identified through sensitivity analyses in Aspen Plus simulations and by referring to the literature[12, 36, 43]. The dominant variables in reactive distillation are: pressure, temperature (threefold dominant: for reaction equilibrium, for reaction rate, and for separation), feed flow rate, feed composition, catalyst activity, space velocity, and reflux ratio. The following sections briefly describe why each variable is dominant.

3.4.3.1 Pressure

Similar to conventional distillation, pressure is dominant for a reactive distillation column since it affects the boiling points of the pure components and azeotropes, given in Table 1. At atmospheric pressure, MA has a lower boiling point than MT. However, at a pressure of 10 atm, the boiling point of MT is lower than that of MA. Consequently, at high pressure, pure MA cannot be produced at the top. Thus, the column pressure must be kept close to 1 atm. This means that the column pressure cannot be independently manipulated.

3.4.3.2 Reflux Ratio

One striking feature of reactive distillation is that there is not only a minimum, but also a maximum reflux ratio for feasibility, achieving high reaction conversion and top product purity. Figure 7 shows how methyl acetate purity and reaction conversion change with reflux ratio. From pilot plant experiments, Agreda and Partin (1984)[36] reported that reaction conversion decreases at reflux ratios above 2.0 (the simulation data plotted in Figure 7 are in agreement with this value and the optimum operating range given below). In the commercial operation of the process the optimum operating range is 1.65 to 1.85, depending on catalyst activity, required production rate and product purity[12].

One qualitative explanation for the existence of this optimal range is the following: if the reflux ratio decreases below the minimum, then AC can appear at the top product due to poor separation. If the reflux ratio is higher than the upper bound, AC comes out at the bottom due to the fact that if we keep increasing the liquid down-flow, we basically re-circulate more and more methyl acetate, and eventually, above the maximum reflux ratio, the system becomes so rich in methyl acetate that the reverse reaction can take place, negating the benefit of separation. Thus, the reflux ratio is a dominant variables since it affects reaction as well as separation performance. However, even if we refer to the reflux ratio as the dominant variable, the variable that is really manipulated is the heat provided to the reboiler, which changes the vapor up-flow to compensate for the changes in liquid down-flow, under a constant distillate flow rate.

3.4.3.3 Temperature

The column temperature profile plays an even more crucial role in reactive distillation than it does in conventional distillation. In fact, similarly to non-reactive distillation systems, the temperature is dominant for separation. But, in reactive systems, as already explained, the separation also prescribes reaction temperature (both thermodynamically and kinetically). Hence, the column temperature profile is also dominant for reaction equilibrium and reaction rate. In a distillation column, both reactive or not, the temperature depends on the pressure, and is changed by manipulating another dominant variable, the reflux ratio.

3.4.3.4 Feed Flow Rate

The feed flow rate, like any other internal flow (i.e. reflux flow), is dominant for the process because it can change desired outputs. However, the set-points of feed flow rate is kept constant to guarantee the desirable productivity imposed on the column by the market, and is only adjusted when required to compensate for changes in market demands or in feed compositions.

3.4.3.5 Feed Composition

The feed composition is dominant since it can affect the reaction conversion. The feed composition can be manipulated by changing either MT or AC flow rate. However, we can only manipulate one feed flow rate in excess since the value for the limiting reactant is fixed by productivity specs. Therefore, the feed composition is not independent of the feed flow rate. Aspen Plus simulations confirm that for a reactive distillation column a small excess of AC (i.e. 5%) has a much stronger effect on increasing reaction conversion than a large excess of MT (>50%). Hence, in case of poor performance, excess AC can give much better compensation than excess MT. However, to achieve this improvement, we pay a price because it is very expensive to recover the excess AC due to the tangent pinch that it forms with W. When we later compare the reactive column (Figure 4) to the distillation column with external reactor (Figure 3), AC excess is used to improve the performances of the latter design when this does not meet the specifications.

3.4.3.6 Catalyst Activity

Catalyst activity is dominant because it can change the reaction rate and therefore affect reaction conversion. In this example, catalyst activity cannot be manipulated, in example by increasing the temperature. However, since the catalyst used for the methyl acetate production system is liquid SA, its activity hardly decays.

3.4.3.7 Space Velocity (Sulfuric Acid Flow Rate)

Space velocity is dominant because it affects reaction conversion. To achieve a higher reaction conversion and corresponding higher MA purity, the flow rate of SA can be increased[12]. However, high SA concentration causes corrosion problem to the bottom section. Hence, the catalyst flow rate can only be changed slightly and it is usually kept at about 1% of the AC feed flow rate[36].

3.5 External Reactors Cascaded into a Non-Reactive Distillation Column

The study of reactive distillation has allowed us to understand what are the limitations of the technology, and how to derive a new design that can be applied to a wider range of industrial processes. In a previous section (3.4.1), we discussed several limitations of a reactive distillation column where reaction occurs inside the column. Table 2 summarizes these limitations. First of all, the temperature range for the separation and the temperature range for the reaction have to match. A homogeneous catalyst is preferable to a heterogeneous one because the latter could cause flow mal-distribution[22] and frequent and costly shut-downs and start-ups to regenerate and replace the spent catalyst. Finally, for a heterogeneous catalyst, space velocity cannot be freely adjusted since it depends on the separation requirements of internal flow rates (reflux rate). As there are upper and lower limits to the reflux ratio, these constrain the maximum amount of catalyst one can put into a column. The need to match both catalyst activity and temperature of the reaction to the distillation strongly limits the applicability of reactive distillation.

All the above limitations can be avoided by going back to the design in Figure 3, where external reactors are cascaded into a non-reactive distillation column[24, 44]. The central idea is the decoupling of the two tasks (reaction and distillation), which gives an increment of available independent practical degrees of freedom. This increment allows us to independently control both reaction and separation temperatures. Furthermore, the needed space velocity can be provided to the process by simply designing *ad hoc* the size of the external reactors, independently of separation requirements. Also, flow mal-distribution, due to the presence of fine catalyst particles in the column, that causes separation and reaction conversion deterioration, is avoided. Finally, with external reactors, complex design of column internals can be eliminated since we can use traditional reaction engineering techniques for designing the external reactors. These advantages are discussed in detail in the next paragraph.

This decoupling results in a design that can be applied when reaction and separation conditions are different and/or heterogeneous catalysts are needed. The external (=side) reactor concept in reactive distillation was introduced in the early eighties by Schoenmakers and Buehler (1982)[45]. Since reaction can be controlled independently of distillation, many applications or derivatives of the side-reactor distillation can be envisioned for heterogeneous catalytic systems. Despite its potential there is little research effort on the design of this side reactor technique[46]. One commercialization is the tert-amyl methyl ether (TAME) production system[47]. Recently, this idea was also applied to the olefin dimerization process[48].

3.6 Comparison of Performance Between Reactive Distillation and External Reactor Column

A conventional reactive tray and a side reactor are sketched in Figure 8. In the side reactor scheme, a liquid stream is withdrawn from the column, fed to the external reactor and then recycled back to the column after being reacted. The return tray in the column is chosen in order to optimize the process performance. Heat exchangers before and after the reactors allow independent control of reaction temperature. Further, it is possible to pack heterogeneous catalysts inside the side reactors and build bigger reactors to have larger space velocities. Replacement or regeneration of spent catalysts can be performed without shutting down the entire column.

The process performance is compared between the side-reactor column and the reactive distillation column by performing, for the methyl acetate example, simulations using Aspen Plus. It is assumed in the simulations that all feed streams to the column, reactive and not, are saturated liquid.

First of all, we chose the optimum location for the four reactors, by changing the location of four reactive trays in a systematic way along the column. Afterward, we inserted the reactors on the column liquid down-flow like by-passes, in other words we withdrew liquid streams from the distillation column and, once reacted isothermally, we fed them back to the trays following the ones from which the streams were withdrawn. The best result obtained was off-specs, about 97.8% MA top purity for RR = 2.2. However, applying some remedies it was possible to reach the desired 99.0%. Based on the analysis of the liquid column composition, we found out that the best location for the return streams from the outside reactors was a few stages above the withdrawal trays, from one to three depending on the reactor. In this way, since the return stages were above the withdrawal ones, we could circulate liquid streams larger than the internal liquid down-flow without drying up the column.

We were able to reach the 99.0% top product purity in the following cases:

1. when the flow rate of the liquid circulated was six times as large as the internal liquid down-flow.
2. when the flow rate of the liquid circulated was three times as large as the internal liquid down-flow and a 5% acetic acid excess was used.

3. when the external reactor temperatures were varied for optimization purposes.

Results are summarized in Table 3. The other remedy previously claimed, increasing the reactor size, cannot be used here as the reaction extent was assumed to reach equilibrium, and for this case increasing the reactor volume does not affect the conversion.

The side-reactor case would also allow us to overcome some problems encountered in the internal catalytic-tray case, especially with heterogeneous catalysts. The two major problems refer to poor reaction conversion and low tray separation efficiency due to the short residence time and flow mal-distribution.

The problem of having poor reaction conversion can be solved for the side-reactor scheme by providing larger catalyst hold-ups, which means larger reactors. On the other hand, lower separation efficiency can arise due to the flow mal-distribution through the column internals packed with solid catalysts. For the side-reactor case the problem is simply not present. In fact, since there is no catalyst inside the column that can cause flow mal-distribution, the separation efficiency is not affected by the use of heterogeneous catalysts. On the other hand, in a reactive column, flow mal-distribution can be only remediate by designing the column with more trays. Therefore, side-reactors are also useful in reactive systems for which low residence time and flow mal-distribution are major problems.

3.7 Summary

We have applied our methodology, based on partial control and concurrent design theory, to Eastman's methyl acetate production system and have derived a counter-current scheme (where side reactors are cascaded into a conventional distillation column) suitable for most reaction systems, where reaction and distillation conditions are mismatched, or for which there are only heterogeneous catalysts available. We showed that this counter-current scheme in reactive distillation circumvents separation limitations due to azeotropes and reaction equilibrium constraints, and can reach performances similar to the reactive column (Table 3).

This example enabled us to understand what are the limitations in current applications, why reactive distillation use is not prevalent yet and what structural changes are needed. In fact, a process must have a catalyst that is active at temperatures that match separation temperature under a specified operating pressure. The pressure, in most cases, has such a strong impact on the boiling points and relative volatility that it cannot be manipulated to change the separation temperature, in order to match the reaction requirements. High catalyst activity is essential to avoiding large hold-ups that would be necessary to achieve desired reaction conversion.

When the catalyst is heterogeneous, we also found that other problems would arise. First, a solid packed in a column requires complex tray internals designed to reduce flow mal-distribution. Then, more trays have to be built to compensate for the deterioration of separation efficiency in the reactive section. Furthermore, each reactive tray has to be designed bigger than a conventional tray to provide large catalyst hold-ups and guarantee sufficiently long residence times. Unfortunately, neither the internal flow rate nor the catalyst hold-up are available as manipulated variables to adjust the space velocity. Finally, it is not possible to perform on-line regeneration and replacement of spent catalysts.

The design of external reactors cascaded into a non-reactive distillation column allows us to overcome all the limitations discussed above, especially when using heterogeneous catalysts. In particular, reaction and separation temperatures can be controlled independently and thus we increase the number of practical degrees of freedom. The temperature in the reactors can be then optimized in order to maximize catalyst activity, and therefore to obtain the highest possible product purity. Continuous catalyst regeneration is possible since we can cyclically shut-down one reactor at a time while operating the rest of them. Furthermore, we can build reactors with large volumes; this allows us to adjust the space velocity independently of separation, by providing more catalyst into the reactors.

However, for the specific example that we considered, the methyl acetate production system, since the temperature ranges for separation, equilibrium and reaction rate perfectly match and the catalyst is homogeneous and very active, the best solution is represented by the reactive distillation column. This is because a non-reactive distillation column with four external reactors, provided with independent temperature control, would definitively be more expensive. On the other hand, this alternative scheme has to be considered as the best option for all those processes that despite showing very strong synergisms between reaction and separation are not feasible in a reactive distillation column because of the insurmountable difficulties due to dominant variables mismatches.

Abbreviation:

AC = Acetic Acid

MA = Methyl Acetate

MT = Methanol

W = Water

SA= Sulfuric Acid

D = Distillate Flow Rate

4. Reactive Distillation Technology in Isomerization Processes

4.1 Introduction

Over the years, the implementation of reactive distillation has been attempted for many different systems and, among these, special attention has been paid to isomerization, especially of light hydrocarbons[25-27]. In this chapter we show the results obtained when we applied our method of evaluating the feasibility of reactive distillation to such systems. In isomerization the difficulty is mainly due to the fact that the reaction is equilibrium constrained and the relative volatility is usually low. Actually, for these processes, complete conversion can be achieved with a simple scheme, such as the one showed in Figure 5, where the unconverted feed leaving the reactor is separated in a distillation column and recycled back to the reactor. Therefore, the application of reactive distillation here is meant to eliminate the cost of the reactor and the recycle, and reduce the reflux ratio, which translates in reducing the heat duty to the reboiler. These savings are balanced by the higher costs of reactive column internals and the costs for research and development. However, even for these systems, the simplification would be convenient whenever it is easy to implement, although very few isomerization processes satisfy the conditions, cited in Chapter 2, for implementing a reactive column.

4.2 Overview

In this chapter we want to show, for several scenarios of isomerization in a reactive distillation column, when the simplification is feasible and what the possible synergisms between reaction and separation might be. For this purpose we took the binary isomerization between normal-hexane (n-H) and 2,3-di-methyl-butane (2,3-diMB) as main example. The two chosen isomers have close boiling points, which makes the separation difficult (Figure 9 gives the boiling points versus the pressure), and all properties are well known.

As already mentioned, the dominant variables are: pressure, temperature, space velocity, catalyst activity, reflux ratio, feed composition, and feed flow rate. The reasons why these variables are dominant are explained in section 3.4.3.

Let us see, for the case when the 2,3-diMB is the desired product, what the analysis of the dominant variables reveal about the process. Matching the operating conditions here refers to the three different conditions for the temperature (separation, thermodynamic, and kinetics), and matching the space velocity with the requirements of the column, dictated by the reflux ratio. We will start analyzing the temperature.

The thermodynamic values for the reaction are:

$$\text{normal-Hexane (n-H)} \quad \overset{\text{Catalyst}}{\Leftrightarrow} \quad \text{2,3-di-Methyl-Butane (2,3-diMB)}$$

$$\Delta H_R^\circ = -2.0 \text{ kcal/mole}$$
$$\Delta G_R^\circ = -0.5 \text{ kcal/mole}$$

The isomerization is exothermic, therefore the desired isomer is thermodynamically favorable at low temperatures, but in order to have an acceptable reaction rate a catalyst is needed. Figure 10 shows the reaction equilibrium composition of the two isomers. At temperatures in the range of 58-69 °C (the boiling points of the two isomers at atmospheric pressure), the composition of the 2,3-diMB is about 70%. As the temperature increases the composition of the 2,3-diMb quickly drops, and for temperatures above 160 ° C the reactant, n-H, becomes the favorable isomer.

This isomolar reaction is assumed to take place only in the liquid phase, so pressure does not have any impact on it, while it highly influences the separation as it determines the temperature profile along the column. Figure 11 shows the relative volatility between n-H and 2,3-diMB as a function of the boiling temperature of a 50/50 mixture of the two isomers (a second scale as a function of pressure is also given in the same figure). At low temperature the relative volatility is acceptable ($\cong$ 1.35), but it drops to unacceptable values as the temperature increases, which indicates that the separation has to be carried out at low temperatures, corresponding to atmospheric pressure.

From the analysis of the temperature it is clear that an overlapped range exists that is valid for both separation and reaction equilibrium, this range is comprised between the boiling points of the two isomers at atmospheric pressure. Therefore, the isomerization is feasible in a reactive column as long as the temperature requirements for kinetics also overlaps the same temperature range. Here, we assume that a catalyst with a high activity is available. In reality no such catalysts exist, present catalysts require higher temperatures, but assuming that a catalyst exists allows us to test the process for synergisms.

Summarizing, the optimum conditions, to carry out the 2,3-diMB isomerization in a reactive column, is to operate at 1 atm, which corresponds to a temperature range of 58 to 69 °C. Showing that the simplification is feasible only concludes the first part of our methodology, we still have to check if it is profitable.

To complete the analysis concerning temperature, we also want to discuss what happens when an overlapped range that satisfies all the requirements does not exist. In order to do this, we consider the same isomerization system, but this time the desired product of the reactive distillation column is n-H instead of 2,3-diMB. From Figure 10, it is clear that we should operate at temperatures above 160 °C in order to convert some 2,3-diMB to n-H. Such temperatures, higher than the case with 2,3-diMB as the desired product, complicate the situation as now we need to increase the pressure in the column so that the temperature range acceptable for the separation also increases and eventually matches the one required for the reaction. We are still assuming that a catalyst with high activity exists, so that the temperature range for kinetics also overlaps the other two temperature ranges. However, it is not convenient to use a homogeneous catalyst (usually the highest boiling component), as it would leave the column from the bottom with the product, which means another separation step is needed to purify the n-H. Assuming that a catalyst exists, for this case, is more realistic because the operative temperature range prescribed by thermodynamics is higher than it is for the mirrored isomerization. But, operating at high temperature (which means high pressure) does not favor reactive distillation because the relative volatility for temperatures above 160 °C is very low (see Figure 11), making the separation difficult to achieve. Therefore, the limitations faced when we want to produce n-H in a reactive column are such as to make the simplification non attractive. To make this point clear, we will also discuss another example of binary isomerization (between cyclo-Hexane and Methyl-cyclo-Pentane). Here the mismatch between the optimum temperature ranges for reaction and separation is much larger, and the disadvantage of using reactive distillation becomes very evident. We will come back to these cases in the examples below.

The matching between the space velocity and the requirements of the column depends on the catalyst available. As we are dealing with an ideal case, and we are assuming the properties of the catalyst, we can consider several reaction rates and explore the matching of these two dominant variables for each case. When the reaction rate is taken to be fast, either approaching equilibrium or approaching 95% equilibrium conversion within the column temperature range, the matching is not a problem because the amount of catalyst needed is small and can be easily filled inside the column. Problems arise when the reaction rate is assumed to be very low, as in this case we might need, to fill in all the catalyst required, a larger volume than available in the column. In the examples section all these cases are treated separately. We will also show the results obtained when we take into account all the problems related to the catalyst, such as deactivation, aging, and flow mal-distribution.

However, for those processes where the three temperature ranges do not overlap each other, or for which the space velocity does not match the column requirements fixed by the reflux ratio, if there are any strong synergistic effects derived from the integration of reaction and separation, we could always use the scheme sketched in Figure 3. With the external reactors cascaded in a non-reactive distillation column, we could provide different temperature conditions for reaction and separation, and at the same time manipulate the space velocity independently of separation requirements.

4.3 Examples of Isomerization for which a Common Range of Temperatures for Separation and Reaction Conditions Exists: 2,3-di-MB Production

In the examples that follow we compare, for several scenarios, the performances achieved when two different designs are used for the same isomerization of n-H to 2,3-di-MB. The first is the design conventionally used for this process, which is composed of a reactor connected to a non-reactive distillation column (shown in Figure 12); the second scheme is represented by a reactive distillation column (shown in Figure 13). Our intent, here, is to see if taking the reaction inside the distillation column can give rise to any synergistic effects, and balance them against the limitations due to the integration. In other words we want to estimate the advantages and the penalties derived from the simplification, in order to understand if, for first order reactions with equilibrium limitations, the cost and the time necessary to implement the reactive distillation technology would be justified.

More specifically, as mentioned before, we analyzed all the aspects involved in isomerization by studying the example for different cases, which are:

1. reaction with a very fast catalyst.

   This case is a limiting case to maximize the advantage of reactive distillation and is not realistic for solid isomerization catalysts. The catalyst activity is considered to be so high that we can actually assume the reaction to be at equilibrium at any stage where catalyst is present.

   For this purpose we take a CSTR at equilibrium as the external reactor and, similarly, the reactive region of the column is also at equilibrium. Taking such a fast catalyst also allows us to neglect all the constraints about the maximum amount of catalyst that we can fit in the column. In fact, since we have an infinitely fast reaction rate, all the catalyst required to achieve the desired conversion could be fitted, if needed, in a single tray and there are no problems of matching the space velocity to the requirements of the column.

2. reaction with finite reaction rate.

   Here, we consider a more realistic case of a catalyst with a finite reaction rate. The external reactor in this case is an isothermal PFR. We also calculate the dimensions of the reactive trays, based on the volumetric vapor flow rate in the non-reactive distillation column[49], to evaluate how much catalyst can be filled in the reactive distillation column. Our goal is to see what penalties are introduced by this new assumption and, in order to have a complete picture of the process, we considered two sub-cases:

   2.a reaction with a catalyst still fast enough to approach 95% equilibrium, at the overlapped temperature range, in the external reactor. In the reactive column space velocity still match quite well with the column requirements, and an acceptable conversion is also obtainable.

   2.b reaction with a very slow catalyst. In this case we assume that the reaction rate is so low that the reaction volume required by the catalyst becomes very large, and a high conversion cannot be obtained in the reactive column. On the other hand, for the external reactor, we can compensate for it by increasing the size of the reactor.

3. presence of an inert impurity in the feed.

   We limited the study of this example only to the case of a very fast catalyst, approaching equilibrium. Since the feed contains an impurity, a purge is required in order to avoid that the inert accumulates in the column; therefore, we want to see how this affects the response. Furthermore the case is different as the number of degrees of freedom in the reactive section of the column is now larger. Here, we are not talking of practical degrees of freedom for control, as defined in Chapter 2, but we refer to the conventional concept of degrees of freedom given by the phase rule: the number of degrees of freedom is equal to the number of components minus the number of phases minus the number of independent reaction equilibrium equations plus 2 (when it is not specified that we refer to "practical" degrees of freedom, it has to always be assumed that we mean degrees of freedom in the conventional way). In fact, when the feed is formed by a mixture of the two hexane isomers, in the reactive region of the column, we only have one degree of freedom. Once the pressure is fixed, the temperature is automatically determined and so it is the reaction equilibrium composition, which does not change from tray to tray, when more than one reactive tray is considered. On the contrary, an inert gives the system a second degree of freedom. So, even fixing the pressure, the temperature can still change through the reactive section, and consequently the conversion also changes. The inert chosen is 2,3-di-methyl-butadiene, whose boiling point (68.6 ºC) is very close to that of n-H (68.7 ºC). In this way we made sure that the impurity leaves the column, either reactive or non-reactive, from the bottom.

At this point we want to underline that the examples evaluated represent ideal cases, because some of the assumptions we made on the dominant variables, especially those concerning the catalyst and its activity, are very strong. But, by making these hypotheses, which favor the reactive distillation, we can understand the reasons for the interactions, if any, between separation and reaction.

4.3.1 Computer Simulations: Assumptions and Procedures

The examples shown in this section have been carried out by performing computer simulations with Aspen Plus. All the simulations, unless otherwise specified, have the following assumptions in common:

1. the pressure is kept constant at 1 atm, and the reaction temperature in the external reactor is fixed at 58 °C (the boiling point of 2,3-diMB), the minimum temperature reached in the reactive distillation column.
2. both distillation columns, reactive and non-reactive, have 40 total trays, the 40th one being the bottom tray, and the 1st being a total condenser.
3. the main product is distilled from the top of the column, while the bottom stream, composed of un-reacted feed and product not separated, is recycled back.
4. the reaction only takes place in the liquid phase. Assuming a two-phase reaction would complex the simulations, but the results would be approximately the same.
5. the total fresh feed is 10 kmol/hr, and it is composed as follows:

   n-hexane (n-H) = 5 kmol/hr

   2,3-di-methyl-butane (2,3-diMB) = 5 kmol/hr
6. a purge from the bottom is also fixed, but for these ideal cases where we have a pure feed, the purge is set to zero. On the other hand, when a feed with a 3% impurity is considered, the purge, taken out from the bottom stream, is fixed at 5% of the feed stream.

The process specification of the external reactor + conventional distillation column design (R+C, Figure 12) is the top purity, which is required to be 99% molar (it would be practically the same on a weight percentage, since the only example where we have an inert impurity in the feed, is when the component chosen has a molecular weight almost equal to that of the isomers, 86 g/mol for the isomers and 82 g/mol for the inert). Since the bottom flow rate is completely recycled to the reactor the yield is also determined. The manipulated variable used to meet the purity specification is the reflux ratio (RR), but the bottom flow rate (B) is also varied to optimize the results. Figure 14 shows, for the case of a reaction with a very fast catalyst, how the RR changes with B (the best location for the feed stage is the 30th tray from the top) and what are its optimum values. In the R+C scheme, the fresh feed is sent to the reactor. The feed tray in the distillation column (the tray whose composition is the closest to the feed stream), to which the stream exiting the external reactor is sent to, is also manipulated in order to optimize the process performances. Figure 15 plots, for the same fast catalyst case, the trend of the reflux ratio versus the feed stage (when B is set to 5.2 kmol/hr, the optimum flow rate), which gives us the best feed stage location. Actually, B and feed stage are manipulated simultaneously following a trial and error procedure.

In the reactive distillation column (RD, Figure 13) we fix the RR, as obtained for R+C, and evaluate the top purity. In this configuration, the fresh feed can only be sent to the column but, similar to the previous design, the process performances are maximized. This time optimum results are more complex to achieve as we can vary not only the feed stage, but we can also change the number of reactive trays and their location. Table 4 summarizes the results when we optimized the performance of a reactive distillation column with a very fast catalyst. While Figure 16 shows, for the same fast catalyst, how the reflux ratio varies with the feed stage, for the RD design, when the only reactive tray is the bottom one. When the product purity obtained is lower (or higher) than required by the specifications, another simulation step is performed. Now we fix the top purity of 2,3-diMB in the reactive column at 99% molar and calculate the RR necessary to reach it.

4.3.2 Discussion of the Simulation Results

In this section we want to discuss the results obtained from the simulations (see Tables 5 through 8).

We can observe that the best location for the reactive region is always at the bottom of the column, where the concentration of the reactant is highest and consequently the conversion is also highest. Having the reactive region located at the bottom of the column means that it is possible to use either a homogeneous or a heterogeneous catalyst. In fact, while a solid catalyst could be fitted only in the reactive region, even if it is in the middle of the column, when a homogeneous catalyst is used, the reactive region goes always from the catalyst feed tray to the bottom tray. Furthermore, we can save on the pumping cost of the unconverted isomer because the recycled bottom flow rate B has no effect in the RD scheme and it is set to 0 (in other words the reactive distillation column only has a rectifying section with a top product and no bottom stream). Otherwise, a positive value for B would mean that we are re-circulating to the reactive tray a stream that comes out from the same stage without changing its composition.

The feed tray is always the stage at which the composition in the closest to the composition of the stream fed to the column. The best feed tray for the R+C scheme happens to be always the 30th. On the other hand, for the RD scheme, the best feed stage location changes from case to case, but it is always one of the reactive trays. For example, the top of Figure 17 shows the liquid composition profile within the reactive column for the case of reaction with finite reaction rate (95% approach to equilibrium at 58 °C). Here the tray whose liquid composition is the closest to a 50/50 mixture of the two isomers is the 37th.

When the catalyst is very fast (Table 5), approach to equilibrium, as mentioned before, the reactive region has only one degree of freedom and the maximum product purity is reached when there is only one reactive tray. In fact, if the reaction region would be formed by several stages, once we fixed the pressure, also the temperature and, therefore, the equilibrium composition are fixed and remain constant in all the reactive trays, but now we are left with less purely distillation trays to perform the separation. In this case there is a very weak integration between reaction and separation, because the reactive column only has 1 reactive stage at the very bottom of the column, while the rest of the stages are purely distillation trays.

When the catalyst is again very fast, but there is an inert, 2,3-di-methyl-butadiene, in the feed flow rate (Table 8), the reactive region in the column has two independent variables. Once the pressure is fixed we still have a degree of freedom and therefore the temperature, and consequently the equilibrium composition, changes along the reactive region, which is formed now by several stages. However, the number of reactive trays is limited by the fact that the column eventually reaches a point at which what we gain in terms of conversion improvement does not compensate for the loss of separation capability, and the top product purity would start to decay. Interestingly, this is the only case where reactive distillation performs, in terms of reflux ratio, slightly better than the two-unit scheme. The reason for this is clearly linked to the presence of the inert. In fact, in the RD scheme, the fresh feed is sent to the bottom tray, and since the inert has a high boiling point, close to that of n-H, it stays at the bottom of the column. In this design there is no recycle, and we get rid of the 3% inert through the purge (5% of fresh feed), which is taken directly from the bottom tray. On the other hand, in the R+C scheme, the purge (again 5% of fresh feed) is withdrawn from the recycle stream (almost as large as the feed rate), which has a large percentage of inert (about 50%). Now, all the inert that is present in the recycle stream and is not purged, the largest quantity, is sent back to the reactor and from this it goes back to the feed stage in the column (30th from the top). From here, the inert has to be separated through the recycle stream and the cycle repeats again. Therefore, the reflux ratio is higher for the R+C design because part of it is used to inefficiently separate all the inert that is then continuously recycled back to the column.

For the case with finite reaction rate (Tables 6 and 7) the composition changes from tray to tray in the reactive region (we have here two degrees of freedom), even if there are no impurities in the feed. The number of trays filled with catalyst is fixed here at the design stage and it is not varied for optimization purposes. Results show that the difference between the two designs becomes large when a catalyst with very low activity is employed. In fact, in the R+C scheme, the specification of 99% product purity can still be achieved with a reasonable reflux ratio by simply using a bigger PFR (cases II and III of Table 7). On the contrary, the amount of catalyst that can be fitted in the reactive distillation column is fixed at the design stage, and the only way we can compensate for having a slow catalyst is to increase the reflux ratio. However, the results eventually blow up and the reactive column needs an unrealistic reflux ratio, order of hundreds, to be able to meet the process specifications (case IV of Table 7). The trend of the reflux ratio with the catalyst activity, for the RD design in case of very slow catalyst, is shown in Figure 18.

To summarize, a general conclusion that we can draw from all the results is that, to our surprise, there are no synergisms rising from the implementation of reactive distillation. If we look at the results of Tables 5, 6, and 8 in terms of product purity (when the reflux ratio is fixed) or reflux ratio (when the product purity is fixed), the reactive column has similar performances compared to the design with separate vessels. In these examples it might be convenient to apply reactive distillation, because the costs for research and development for more complex column internal, and, in some cases, for higher heat duty to the reboiler, are balanced by the savings of the reactor and the pumping costs. However, we want to remind the reader that the examples are all based on the strong assumption that a catalyst exists active at such low temperatures (58-69 °C).

On the contrary, for very low catalyst activity (see Table 7), which could be due not only to a slow catalyst but also to phenomena such as aging and deactivation, the scheme with the external reactor actually outperforms the reactive distillation column. In this case, which is more realistic, we could compensate for low reaction rate in the external reactor, but not in the reactive column.

For the case of very fast catalyst, we also tried lowering the number of total trays to 20. By doing that we wanted to see if a more complex to achieve separation, since there are fewer distillation trays, would have shown any interactions between the two unit operations. The results obtained (Table 9) are similar to what obtained with the 40 trays column (Table 5). The number of trays was not further reduced because we need enough trays for the separation to take place and with a real catalyst we also need enough volume to fit it in and to provide sufficiently long residence times.

4.3.3 Simulations with Heterogeneous Catalyst

In this example we want to show limitations that only applies when the catalyst used in the reactive column is heterogeneous. For this specific problem we only consider the case of a catalyst that reaches 95% equilibrium conversion at 58 °C. Here, we want to depict a more realistic situation in which the presence of a fine solid, packed inside a distillation column, causes problems of flow mal-distribution, which not only reduces the separation efficiency, but also deteriorates the reaction conversion. For this purpose the number of ideal trays composing the reactive distillation column is lowered from 40 to 30, out of which 15 are filled with catalyst.

For the R+C design, this limitation does not apply, as the catalyst is only present in the reactor and not in the column. Furthermore, a PFR with a larger volume allows us, once again, to reach high reaction conversion. On the other hand, the only way to compensate for this limitation in the RD scheme is to increase the reflux ratio. Table 10 shows that under these more realistic assumptions, finite reaction rate and low separation efficiency, the R+C scheme definitely outperforms the RD configuration, as the reflux ratio of the latter increased by 80%. Therefore, in this example we need to provide to the reactive distillation column almost twice as much heat, the main cost in a distillation column, as compared to the two-unit design.

4.4 Cases for Which the Ranges of Optimum Temperatures for Reaction and Separation Do Not Match

To complete the study of first order reaction systems with equilibrium constraints, as mentioned before, we also want to present results of processes for which the operative conditions do not match. By doing this we intend to numerically quantify, in terms of reflux ratio, the advantages of keeping the two unit operations separated.

4.4.1 normal-Hexane Production

As first example we studied the same n-H/2,3-diMB isomerization system, but this time the desired product is the higher boiling isomer n-H. If we look at Figure 10, we see that in order to convert the 2,3-di-MB to n-H the reaction should be carried out at temperatures higher than 160 °C. But, because of the relative volatility that quickly drops as the temperature increases (Figure 11), the distillation columns, both reactive and not, have to be operated at atmospheric pressure, this also fixes the column temperature profile (58-69 °C). On the other hand, the temperature in the external reactor can be chosen freely, and we set it at 250 °C, which requires a pressure of 40 atm in order to assure a liquid-only inventory (the reactive phase) in the reactor. While these conditions do not represent a problem for the two-unit design, where the operating conditions for reaction and separation are fixed independently, they strongly limit the performance of the reactive column.

For this example we only simulated the case with very fast catalyst (approaching equilibrium), where the feed is the usual 50/50 mixture of the two isomers without any impurity, so that the purge is set to zero, and both columns have 40 total trays.

Table 11 summarizes the results for this example. The locations of the feed trays are mirrored with respect to the case with the 2,3-di-MB as desired product. In the reactive column the feed tray is the 2nd from the top, the first tray is a total condenser, which is also the only reactive tray. The reasons that explain the optimum number of reactive trays and the best location of the feed stages are similar to those for the previous case.

The numeric results show that for this example the advantage of having the two units separated, expressed in terms of heat duty supplied to the reboiler, becomes significantly large. We have to provide to the reactive distillation configuration almost 50% more heat than to the non-reactive column. For a comparison, it could be noted that, for the mirrored case (2,3-di-MB as desired product), the reactive column only required 10% more heat than the two-unit scheme (Table 5).

4.4.2 cyclo-Hexane/Methyl-cyclo-Pentane Isomerization

The second example of first order reactive systems with equilibrium constraints is another binary isomerization system, but this time the reaction equilibrium has a much stronger temperature dependence (Figure 19). The selected isomers are the cyclo-hexane (boiling point: 81.4 °C) and the methyl-cyclo-pentane (boiling point: 71.5 °C).

The thermodynamic values for the reaction, when the cyclo-hexane is selected as desired product, are:

$$\text{Methyl-cyclo-Pentane (M-c-P)} \quad \overset{\text{Catalyst}}{\Leftrightarrow} \quad \text{cyclo-Hexane (c-H)}$$

$$\Delta H_R^\circ = -3.9 \text{ kcal/mole}$$

$$\Delta G_R^\circ = -1.0 \text{ kcal/mole}$$

Similar to the case studied in section 4.4.1, we only considered the very fast catalyst with the reaction approaching the equilibrium conversion. Both columns have 40 total trays, operate at atmospheric pressure, and the feed is a 50/50 mixture of the two pure isomers, hence, the purge is still set to zero.

In this case, unlike the n-H/2,3-di-MB isomerization, the formation of the higher boiling component, c-H, is favored at low temperatures. Therefore, for completeness we want to quickly discuss the results (Table 12) also for the c-H production (for which a common temperature range for separation and reaction exists). The temperature in the outside reactor, independently adjustable, has been fixed at 50 ºC. c-H, the higher boiling component, leaves the column from the bottom, and therefore it requires a heterogeneous catalyst. In the non-reactive column the fresh feed is sent to the 5th tray from the top, while in the reactive column it goes to the 2nd tray (the only reactive tray), the first distillation stage (also in this case the top tray is a total condenser). Once again, even if there are no synergistic effects, if a catalyst exists, it could be convenient to implement reactive distillation, as the costs for research, more complex column internal, and a slightly higher reflux ratio (10%), are balanced by the savings of the reactor and the pumping costs.

However, the main reason for studying this isomerization is when we want M-c-P as the desired product. The results for this example are summarized in Table 13. The feed stage is located in the bottom section, the 34th tray for the non-reactive column and the last one for the reactive column, still the only reactive stage.

In this case, having such a strong dependence of reaction equilibrium on temperature means that operating the outside reactor at higher temperature will assure a much larger conversion, highlighting the advantage of using the two-unit design. In fact, setting the temperature in the outside reactor at 300 ºC gives a very large difference in terms of heat provided to the reboiler, as the reactive distillation column now requires a heat duty 2.6 times larger than the conventional column. Of course, such a difference cannot be compensated by saving the reactor and the pumping costs. This example shows that the implementation of reactive distillation for highly temperature dependent reactive systems is not advisable when the operating conditions do not match.

4.5 Advantageous Application of Reactive Distillation

The results obtained in this chapter demonstrate that there are no synergisms when using a reactive distillation column for a first order reaction with equilibrium limitations. Nevertheless, since reactive distillation, when applicable, has potential for large cost reductions, we want to show now a feasible and useful implementation of reactive distillation.

Let's assume we have a non-reactive column, which is used to separate a higher value component from a feedstock, and complete separation is not economical; these cases are quite common in industry. As an example we use the same n-H/2,3-diMB binary system with 10 kmol/hr feed, 50% each isomer. In a 40-tray distillation column we separate the 2,3-di-methyl-butane from the top at 99% purity. Table 14a displays the results, in terms of reflux ratio and feed stage, when the distillate flow rate is set to 5 kmol/hr (50% of the total feed). Now we take the slowest catalyst from the previous examples, the one used in case IV of Table 7, and we simply fill it into 20 trays of the distillation column, and see how much the productivity increases. In the reactive column obtained in this way, we simply fix the top purity at 99% and the reflux ratio as from Table 14a, while the distillate flow rate is free to change. Results are still optimized by changing the locations of the reaction region and the feed stage. For this case the productivity increases about 75%. Table 14b shows the results.

This example shows a potential application for reactive distillation technology. In fact, since the column already exists and operates, the increment in yield that can be obtained is large enough to exceed the expenses necessary to implement the reactive region, even for slow and aging catalysts. This procedure is used, in industry, in the process to separate iso-butane from n-butane.

4.6 Summary

In this chapter we applied our methodology to first order reactive systems with equilibrium constraints to check the applicability of reactive distillation technology. As examples we considered isomerization processes.

In terms of design, these examples are much simpler than the methyl acetate one studied in the previous chapter, as the processes can be carried out in a simple design where a reactor is connected to a distillation column with recycle of the unconverted reactant back to the reactor (Figure 12). For these examples the only simplification possible is to bring the reactor inside the column.

In order to have a set of results as complete as possible, we considered examples of isomerizations when the operating conditions match as well as cases for which they do not match. We studied a variety of cases where we assumed different properties for the catalyst, different feed compositions, and different temperature dependence for the reaction equilibrium.

Generally, the driving force for process simplification is economic. Here, all we can save is a reactor, therefore, unlike the methyl acetate system, we cannot afford to pay large penalties in the simplification. However, the reactive distillation technology would be a valuable option if the simplification would actually show strong synergistic effects, leading to significant performance improvements. Therefore, for all the examples, we checked for the existence of any synergistic effects between separation and reaction. And in order to do so, we compared, for several scenarios, the performances of a two-units scheme (conventionally used for a first order reaction with equilibrium constraints) to the performances of a reactive distillation column. The synergisms that we could expect are one or a combination of the following:

- lower reflux ratio (which means a smaller reactive column and mostly less heat to be provided to the reboiler, the main cost in a distillation column).
- smaller amount of catalyst.
- reduced recycle flow rate (which reduce the pumping costs).

As first example we considered the binary isomerization of n-hexane (n-H) to produce 2,3-di-methyl-butane (2,3-diMB). The example was analyzed for several cases, such as: reaction with a very fast catalyst (approaching equilibrium); reaction with finite reaction rate (at several different catalyst activities); and reaction with a very fast reaction rate and an inert impurity in the feed. For the fast reaction rate we also considered lowering the total number of trays in both columns, and finally, for the same catalyst, we took into account flow mal-distribution, which deteriorates both the reaction and the separation, in the reactive region due to the presence of a heterogeneous catalyst. Since the main cost in a distillation column, reactive or not, is the cost of the heat to be provided to the reboiler, we based our comparison on this variable, and therefore on the reflux ratio.

Surprisingly, in all these cases (Tables 5-10) the reactive column never showed any synergisms. However, for the cases shown in Tables 5, 6, 8 and 9, the penalties suffered are limited, therefore reactive distillation could be implemented (given that a catalyst exists active at such low temperature range: 58-69 °C).

On the other hand, the results summarized in Tables 7 and 10 show that for more realistic cases (slow and aging catalyst, and flow mal-distribution) the two-units scheme outperforms the reactive distillation column, which does not represent an option.

In a second series of simulations we took into account systems for which the dominant temperatures do not match each other. We studied again the n-H/2,3-diMB reaction when the n-H is the main product. In this case we found out that not only the reactive distillation does not show any synergisms, but the advantage of keeping the two unit operations separated is very large (Table 11). To make this point even more clear, we considered another binary isomerization, c-H/M-c-P, which has a much stronger temperature dependence. The advantage of R+C design here is undisputable, since the heat duty required is 2.6 times smaller than the RD configuration (Table 13).

However, if there would be processes with strong synergistic effects between separation and reaction for which the dominant variables do not match, we could use the distillation column with side-reactors shown in Figure 3.

Finally, in the last example of the simulation results, we showed a very valuable implementation of reactive distillation when we already have a non-reactive distillation column. This application simply consists of fitting some catalyst within the existing distillation column. At this point, even if the catalyst is slow and it ages, it does not matter because whatever increment we get in productivity is a clear gain (Tables 14a and 14b).

Abbreviation:

n-H = normal Hexane

2,3-diMB = 2,3-di-Methyl-Butane

c-H = cyclo-Hexane

M-c-P = Methyl-cyclo-Pentane

RD = Reactive Distillation Column

R+C = External Reactor + Conventional Distillation Column

RR = Reflux Ratio

B = Bottom Flow Rate

5. Discussion and Conclusions

The main goal of this thesis was the development of a methodology that can be used to understand, in a reliable and systematic way, before investing large amounts of time and money in research, if process simplification (as defined in Chapter 2) can be successfully applied to a new process. The need for realizing such a tool was suggested to us by studying reactive distillation. As mentioned earlier, this technology saw a few spectacular implementations in the eighties[11-15]. Since then, a large number of potential applications of reactive distillation has been filed in patents or published in articles[21-23], but very few full-scale plants have been built. The formulation of this theoretical framework also allowed us to explain the reasons why the number of successful applications of reactive distillation has been so limited and to suggest how to efficiently look for new applications. A last goal of this thesis was the development of a new design (sketched in Figure 3) that allows us retaining most of the advantages of reactive distillation when this cannot be implemented[24].

Our work is based on two methodologies previously developed. The first is a method for differential economic evaluation of new processes[1-2] developed by Prof. Shinnar and co-workers. This method evaluates the advantages of a new process in a comparative way. The new process proposed for development is compared to the conventional process used for the same product, and only the differences between the two processes are analyzed for evaluating the potential advantage of the new design. The other theory used in our thesis, the concurrent design[3-10], was developed by Profs. Shinnar and Rinard and co-workers, and it deals with design and scale-up of new processes. This methodology focuses on identifying and analyzing the dominant variables of a process, which are either internal flows or state variables, whose impact on the outputs and stability of the system is strong[7-9]. Safe scale-up and good controllability require that all the dominant variables have to be independently controllable over a sufficiently wide range.

When designing a new process, an important task that one has to accomplish, while developing design alternatives, is to correctly identify and study the impact of the dominant variables on the process. Examples of dominant variables are: temperature, pressure, space velocity, reflux ratio, key component concentration, etc.. This task is important because in order to achieve stable steady state operation, or in other words the ability of meeting the desired specifications, the dominant variables have to be independently controlled. The success of our methodology depends very much on the correct analysis of these variables.

The dominant variables in a reactive distillation column are space velocity, catalyst activity, feed flow rate, reflux ratio, feed composition, temperature, and pressure. Temperature and pressure are dependent on each other so only one can be fixed. The problem is that temperature is dominant for several aspects: reaction rate (or kinetics), reaction equilibrium (as it determines the equilibrium composition), and separation (as the relative volatilities are a function of temperature and pressure). It is quite common in both chemical reactions and separation processes that one dominant variable has a strong impact on several outputs, and ref. 9 discusses how to handle that. The most severe penalty of combining a reactor with a separation process is that the desired range of values of one dominant variable may be totally different for the reaction and the separation.

In process simplification, the analysis of the dominant variables is even more crucial than it is for other processes, because the integration can only be performed if the range of acceptable values of the dominant variables, for all the unit operations involved, match each other. And, when one variable is dominant for several aspects, a common range of acceptable values has to exist that satisfies all the requirements.

The two matches that have to be assured, in order to implement the reactive distillation technology, are the matching of the three requirements for the temperature, and the matching of the reflux ratio, and therefore column diameter and number of stage, with the space velocity. A common problem to any process simplification is the reduction of the number of independently controllable dominant variables.

The matching of the temperature requirements is the most difficult one. In any reactive system, the temperature range for the reaction is given by matching the temperature range desirable for improving the equilibrium with the temperature range within which the reaction rate is acceptably large, which depends on the available catalyst. In reactive distillation the matching of the temperature requirements is even more complex because now we also have to match the temperature range required for separation, which is fixed between narrow limits. There are very few processes for which the acceptable values of these three temperatures overlap each other, over a sufficiently wide range, and this is the main reason why reactive distillation has seen so few applications.

The other matching is between the requirements of the column with the space velocity. The diameter and number of stages (therefore height) are fixed by the requirements of separation. This gives a finite volume for the catalyst. If the volume available for the catalyst is not sufficient, it would be cheaper to have an external reactor than increasing the volume of the column.

However, there are examples where the dominant variables do not match, but there are such strong synergisms between reaction and separation that would significantly improve the process, synergisms that we want to retain. In this case the only option we have is to modify the design. But, changing the design does not change either the number or the type of dominant variables, as they only depend on the process itself and not on the specific design developed. What we can do, by modifying the design, is to increase the number of values at which these variables can be independently controlled[8] or disengage two dominant variables regaining, in this way, the practical degree of freedom lost because of the simplification[24].

For example, in the fluidized catalytic cracker (FCC) discussed in refs. 3-10, it is sometime desirable to increase the temperature difference between the bottom of the riser and the top. This can be achieved by providing the feed to the riser reactor in stages, and is done to increase olefins yield and octane[7, 9]. Feeding the riser in stages does not change the number or the type of dominant variable, but now we can fix the temperature at different values along the riser reactor by manipulating the feed flow rate at each inlet. Another example is the design shown in Figure 3 where a conventional distillation column is connected to several external reactors. The dominant variables are the same as for the reactive distillation column (both designs are used for the same process), but now the temperature of the reaction and the temperature of the distillation are disengaged, and we can fix them independently. Also the space velocity does not have to be matched with the column requirements, because we can now fix the reactors' volume independent of separation. This design, unlike a reactive distillation column, has the potential to be applied to many processes because the main limitation to the implementation of reactive distillation technology (the matching between the operative conditions of reaction and separation) has been removed.

In order to understand all the features involved in reactive distillation and being able to properly develop our methodology, we considered two examples very different from one another. In the first case, the methyl acetate production system, there are very strong synergisms rising when the reaction and the separation are integrated in a single vessel. On the other hand, in the second example, we dealt with a simpler class of processes, first order reactive systems with equilibrium limitation, that shows very weak or no synergistic effects at all.

A very strong synergism that one would expect when implementing a reactive distillation column is that the preferential removal of the product from the catalytic region shifts the reaction conversion beyond the limit fixed by the reaction equilibrium. But, analyzing the various examples studied, we realized that this synergism does not hold in general, but it depends on the process. It is important to understand that no matter how efficient the separation is, a reactive distillation column can never act like a membrane reactor. What we mean is that a membrane physically removes a compound from the reactive system, shifting the conversion further than the reaction equilibrium alone would allow. In reactive distillation, in order to achieve efficient separations we need to design several trays. The products that we want to distill or condense out from the column have to go through several stages, including the reactive stages, before they can actually be removed from the unit.

This can be especially penalizing for a binary reversible reaction, or a multi-component reversible reactive system with only one product, when relative volatility is low and we have a finite reaction rate. As, for these systems, the separation is very slow and the catalytic region is quite large. Therefore, once formed, the desired product is not quickly vaporized, and its concentration builds up in the liquid (reactive) phase of the catalytic region up to an extent limited by the reaction equilibrium.

Let us consider, for example, the n-H to 2,3-diMB binary isomerization. The plots in Figure 17 show that the magnitudes of the liquid and the vapor composition profiles are very similar. This is due to the low relative volatility between 2,3-diMB and n-H (Figure 11). Furthermore, since the reaction rate is finite, it takes 20 reactive stages, in the bottom half of the column going from stage 40 to 21, to achieve a sufficiently large conversion. A high product purity is only achieved with high reflux ratios. This means that the distillation does not improve the reaction conversion.

On the other hand, for reversible reactive systems with multiple products (among which the desired product has to be either the lowest or the highest boiling component if we want to perform the process in one column) the equilibrium reaction could only be limiting if all the products are present in the reactive phase of the catalytic region in large quantities at the same time. Therefore, these systems would not suffer from this problem, at the same extent, if at least one product can be preferentially removed from the liquid phase. This is the case for the methyl acetate reaction system, where the conversion would be constrained only when sufficiently large amounts of both methyl acetate and water are present in the liquid phase of the reactive region at the same time. But, as shown in Figure 20, the methyl acetate moves toward the top section (its concentration in the liquid phase is very high only at the top of the column), while the water moves toward the bottom (the concentration in the liquid phase becomes high at the very bottom of the column). Therefore the two products are never present in sufficiently large quantities in the liquid phase at the same stages. The preferential removal of methyl acetate here has a large impact on the process, and the reaction can actually reach conversions larger than the reaction equilibrium. In this case the separation enhances the reaction.

Before discussing the two classes of examples studied, we want to briefly summarize our methodology. First of all, we have to thoroughly analyze the process we are studying, and characterize it in terms of all the constraints and limitations involved, such as azeotropes formation, pinch points, reaction equilibrium limitations, occurrence of side reactions, potential impact of impurities or corrosive compounds, etc.. Then, we proceed with the development of design alternatives. Once a design that is able to meet the specifications has been determined and all the dominant variables of the process have been identified, we have to analyze them in order to check if they match and whether or not it is possible to perform any process simplification. Finally, if the integration is feasible, the potential advantages are to be weighed against the penalties suffered. When properly applied, this methodology allows us to achieve correct results even before performing any computer simulation or actual laboratory experiment. In fact, in our method, computer simulations and laboratory scale experiments are used to prove the conclusions, not to draw them.

Let us start the discussion of the results from the simpler processes, the binary isomerization cases, which were chosen as examples for first order reactive systems with equilibrium limitations. As there are no industrial processes using reactive distillation for either isomerization or a first order reactive system, we chose a hypothetical case, binary isomerization of normal hexane to produce 2,3-di-methyl-butane. In this case, a reactor followed by a conventional distillation column with the recycle of the unconverted isomer back to the reactor (Figure 12) can meet the specifications. The only improvement we can reach is to take the reactor inside the column, therefore the synergistic effects that we can expect, beside saving the reactor, are: the reduction of the recycle stream of the unconverted reactant, with savings on the pumping costs; and the reduction of the reflux ratio, or in other words the reduction of the heat to be provided to the reboiler, which represents the main operating cost in a distillation column. These synergisms have to be weighed against higher costs of column internals, time and money for research and development, loss of practical degrees of freedom, and all the problems discussed about the catalyst (section 2.4). Since the potential advantages are not very large we cannot afford to suffer large penalties.

Once the design has been chosen, we proceed with the analysis of the dominant variables. Both reaction equilibrium (Figure 10) and separation coefficients (Figure 11) require a low temperature range (58-69 °C, the boiling points of the two isomers), therefore the simplification is feasible if a suitable catalyst exists. Since we are dealing with an ideal case, we assume that such a catalyst exists. Considering different reaction rates allows us to study their impact.

Next we compared, for several scenarios, the results of a reactive column (Figure 13) to a conventional two-unit design (Figure 12).

To our surprise we found no synergisms whatsoever for reactive distillation.

When we optimized the distillation column for a fast catalyst, approaching to equilibrium, we found the catalyst should be confined to one tray close to the bottom (Table 5). What it means is that the reactive distillation column is practically a separate reactor in the bottom and a distillation column above it. However, there is no question that if we have a catalyst that allows us to do this then it would be convenient, but this is very seldom the case.

If the catalyst has a finite reaction rate, there is always a penalty for the integration, as in this case (Table 7), to get the same product purity, we need a much higher reflux ratio, as the reactive section of the column contributes little to the separation.

Problems of poor separation and low reaction conversion, due to flow mal-distribution caused by a solid catalyst, also make the reactive distillation not attractive, as we need now a reflux ratio almost twice as big as compared to the conventional scheme.

Now let us look at the requirements for successful applications:

1. There has to exist a temperature range, reasonably wide, that satisfies all three conditions for:
    a. favorable reaction equilibrium.
    b. favorable separation coefficients.
    c. sufficiently high reaction rates.
2. The catalyst has to be sufficiently active such that it fits into the distillation column without excessively enlarging it.

3. The catalyst has to be stable and its activity has to remain high for a sufficiently long time.
4. For a homogeneous catalyst the desired product has to be the lowest boiling one.

Actually, membrane reactors have similar problems. The membrane has to be selective and efficient at the temperature of the reactor. Suitable membranes for dehydrogenation of iso-butane to iso-butene (explained in Chapter 2) and, especially, steam reforming for hydrogen production would be very desirable, as both cases mentioned have reactions that are strongly equilibrium constrained. However, present membranes are not selective at the required temperatures.

One significant difference between reactive distillation and membrane reactors is that, due to the higher potential of the membrane reactors, a large research effort would be justified. On the other hand, in reactive distillation, all that can be achieved are some savings in capital cost, and one has to weight the high cost of research and development for a new catalyst versus potential savings.

If normal hexane is the desired product, the dominant variables do not match. If we set the column temperature at the conditions optimal for the separation (58-69 °C) then the formation of the undesired isomer in the catalytic region is favored. If we fix the temperature in the column to satisfy the reaction requirement (200-250 °C), we need to increase the pressure. This reduces the relative volatility making the separation very difficult. Figures 10 and 11 show this mismatch. From the simulations result that, similar to the mirrored case, the integration between separation and reaction is also very weak, as the only reactive tray is located, this time, at the top of the column. In this case, the advantage of the two-unit scheme is very clear (Table 11). This advantage increases with the dependence of the reaction conversion on temperature, as shown in the cyclo-hexane to methyl-cyclo-pentane isomerization. Here the reflux ratio for the reactive column is 2.6 times as big as for the conventional scheme (Table 13). The fact that reactive distillation is not an option for these examples could have been seen, applying our methodology, by only analyzing the dominant temperatures, and noticing that the required operating conditions for separation and reaction do not match.

There are, however, interesting applications even if the conditions for successful implementation are not fulfilled. Consider an isomer separation column, where there is no reaction and the undesired isomer, once separated, is sold. If one can put some catalyst into a section of the column (bottom section for a low boiling desired isomer) one can get additional yield of the desired isomer at a low cost. Even if the catalyst ages before the turn-around (any unit is shut down at fixed intervals, 2-3 years, and inspected and repaired. A catalyst should last for the period between two turn-arounds, otherwise the replacement would have a significant incremental cost), or yield is low, one still can make a nice profit without large investments. Results of such application, for the n-H/2,3-diMB system, are shown in Tables 14.a and 14.b. This application can have significant savings, and we are aware of some unpublished realizations. But a high yield would still require a separate reactor.

Our results explain why the effort for finding suitable applications for reactive distillation for mono-molecular or pseudo-first order reactions has not had any full-scale implementation.

The conclusions change completely for the methyl acetate production, a quaternary reactive system with much stronger limitations. In this process, due to the presence of two minimum boiling azeotropes (methyl acetate/water, and methyl acetate/methanol), pure methyl acetate cannot be produced in a simple scheme with a reactor followed by a non-reactive distillation column (Figure 6), for any excess of one of the reactants.

If the two reactants are immiscible one can get complete conversion of one reactant by using a counter-current reactor with excess of the other reactant, similar to what is done in multi-stage extraction processes. However, the methyl acetate reactive system has miscible reactants, therefore one cannot build such a counter-current reactor train for it. What one would have to do is put a separation process between each of the two reactors. Figure 2 shows such a scheme for a case where the components are separated by distillation. This scheme can prevent the formation of the methyl acetate/methanol azeotrope (a product/reactant azeotrope) by complete conversion of methanol, avoiding much more complex schemes. Also the azeotrope between methyl acetate and water (a product/product azeotrope) can be broken by extractive distillation. Luckily, acetic acid, a reactant, also works as extractive agent.

A simplification can be obtained by noticing that all the reactors and distillation columns in Figure 2 are fed with the same compounds, it only changes the composition along the reactor train. This allows us to put all the distillation columns together, if they are not too tall, in order to form the design shown in Figure 3. One important synergism here is the ability to carry out a counter-current reaction with miscible reactants.

Our investigation of the dominant variables showed that the design in Figure 3 could be further simplified, as the optimum ranges for the three temperature requirements match each other over a sufficiently wide range of values, allowing us to bring the reactors inside the column. With this final step we could realize the reactive distillation column in Figure 4. This scheme can circumvent both azeotropes in the same ways the schemes in Figures 2 and 3 do, and it is able to meet the specs.

Azeotropes can sometime be circumvented in other ways. If the desired product is the highest boiling component, while the azeotrope has a low boiling point, then the product can be removed from the bottom and the azeotrope from the top with the by-product. The azeotrope could be successively separated from the by-product and recycled to the column; this happens in the butyl acetate production system[50]. We did not consider it necessary to investigate all possible examples, because once one understands clearly what the limitations are and what one really wants to achieve, then the possible design options become quite obvious, and our methodology can be applied in a straightforward way. However, practically all well-known industrial realizations of reactive distillation deal with elimination of azeotropes[12, 14, 15].

Still, in all such cases, one is limited by the same constraints that one faces in the first case we discussed and it is quite rare that the penalties of integrating distillation and reaction into one vessel are not so large as to make the process unattractive.

An important contribution of our work was to show that one could still get all the advantages of reactive distillation by using the scheme in Figure 3, in which the distillation columns have been combined into one tall column with several external reactors. We showed that if the conditions are such that a reactive distillation column will achieve these goals, the scheme in Figure 3 could also achieve this (Table 3).

While this is no longer reactive distillation it is still an important tool for process simplification. For example, if the methyl acetate production system would not have had a catalyst useful for reactive distillation, or many of the other conditions would have been violated, the scheme would still have been much cheaper than the conventional scheme in Figure 1.

This is an important result as it opens a new area of research and development of process simplification, for processes that have complex reactions that result in products that are hard to separate due to the formation of azeotropes.

In the methyl acetate production system everything works out well, and the synergistic effects acquired with the process simplification are very strong. This example was particularly useful because it allowed us to learn how to find new ways of integration to simplify a process. In fact, we could understand that in a multi-reactants system, a product/reactant azeotrope can be circumvented by complete conversion of the reactant, if the two reactants are fed counter-currently. While a product/product azeotrope can be broken by extractive distillation (which can be performed in the same reactive distillation column). From this conclusion we have been able to obtain a new and efficient process configuration, the counter-current non-reactive distillation columns with external reactors cascaded in it (Figure 3). The importance of this design is that, since it was not obtained by matching the dominant variables of the process, it does not suffer from all the limitations of reactive distillation (although it still retains the advantage of breaking azeotropes, and reaching conversions higher than reaction equilibrium) and it is able to meet high purity requirements. This design, as mentioned before, has a much higher potential to be successfully implemented than the reactive distillation technology, because it is applicable to all those reactive systems with complex separations for which the reaction and the separation conditions do not match.

Despite the fact that this design methodology has been proved by considering all examples dealing with reactive distillation, having understood the methodology, this tool can be safely applied to any other process simplification. This tool, properly applied, allows a designer to save both time and money without affecting the correctness of the conclusions drawn. Finally, we would like to remark again the pivotal role that a correct identification and analysis of the dominant variables plays in this methodology.

Appendix

A.1 Simulation Procedure for the Methyl Acetate Example

A.1.1 Reactive Distillation Column

The state equation used in the "Properties" menu in Aspen Plus is "Wilson-NTH", appropriate for non-ideal miscible systems.

The distillation column is a "RadFrac", chosen from the "Columns" menu in the model library, operated at 1 atm. It has a total of 60 ideal trays, with the top one, stage # 1, being a total condenser. The process has 2 reactants, fed separately and stoichiometrically (except when otherwise specified), which are both pure saturated liquid at atmospheric pressure. The acetic acid feed (1000 kmol/hr) is sent to the 10th tray, while methanol feed (1000 kmol/hr) is sent to the 50th tray. The reactive region goes from the 12th, down to the last tray, the 60th.

The reaction, which takes place in the liquid phase, is supposed to reach equilibrium, with the following equation[43]:

$\ln(K_{eq}) = 0.83983 + 782.98/T$

The simulations are run by fixing the distillate flow rate at 1000 kmol/hr and for different reflux ratios. The concentration of methyl acetate in top distillate stream (product specification, it is required to be 99.0 mole %) and the reaction equilibrium conversion are the results.

A.1.2 Distillation Column with External Reactors

The property and the feed are the same as in the previous case, and we initially take a non-reactive 60-tray column.

To choose the best location for the 4 external reactors, we fix the distillate flow rate again at 1000 kmol/hr. Then we take into the column only 4 reactive trays, not necessarily consecutive, and move them up and down in order to maximize the top product purity. The reflux ratio is also varied for optimization purposes. The best locations for the 4 reactive stages are trays # 38, 46, 49, 56.

Afterwards, 4 external CSTR reactors are connected to the non-reactive column, and used as by-passes at the same locations as the reactive trays (38, 46, 49, 56). The withdrawn stream have to be increased little by little and one at the time to prevent that large changes in the internal flows dry-up the column.

Then the locations of the return trays are manipulated in order to optimize the top purity. The best locations for the return stream are trays # 35, 44, 47, 54.

To meet the 99% top methyl acetate purity specification the following remedies are applied:

1. the withdrawn stream flow rates are increased to 6 times as large as the internal liquid down-flow (since the return stream from the reactor to the column goes to an upper tray the column does not dry-up).
2. the withdrawn stream flow rates are increased to 3 times as large as the internal liquid down-flow, and a 5% acetic acid excess is considered.
3. the operative temperatures of the 4 external reactors are optimized and fixed, from top to bottom, respectively at 55, 60, 60, 65 °C.

A.2 Simulations Procedure for the Isomerization Examples

A.2.1 Production of 2,3-di-Methyl-Butane

The state equation used in the “Properties” menu in Aspen Plus is “Peng-Robinson”, appropriate for hydrocarbons.

The simulations compare the performance of a reactive distillation column (Figure 13) with the performance of a reactor + non-reactive distillation column scheme (Figure 12). Both columns (RadFrac), operated at atmospheric pressure, have 40 total ideal trays, with the top one, stage # 1, being a total condenser.

A.2.1.1 Very Fast Reaction Rate, Approach to Equilibrium

Unless otherwise specified the feed is a 50/50 mixture of the two isomers (5 kmol/hr each, 2-3-di-methyl-butane and normal-hexane). The main product is distilled from the top, while the bottom product is recycled (to the reactive column in Figure 13 or to the external reactor in Figure 12). A purge on the recycle stream is also considered (it is equal to 0 kmol/hr when the feed has no impurities). The external reactor is operated at 58 °C (minimum temperature in the reactive column) and at 38 °C (as the reaction temperature is independent of distillation).

We assume the reaction, which takes place in the liquid phase, to reach equilibrium. The external reactor is a CSTR. In this example an equation for the reaction equilibrium is not available and we use equilibrium based on the internal database of Aspen Plus.

The simulations are performed in two separate steps.

In step 1, we fix in the 2-unit scheme the top 2-3-di-methyl-butane purity at 99% (product specification) and the bottom normal-hexane purity (since this is not a specification we change its value, from run to run, for optimization purposes). The two manipulated variables used to meet the spec are the bottom flow rate and the reflux ratio. To optimize the results the fed stage is also varied.

In step 2, we fix in the reactive column the reflux ratio and the recycle stream as obtained in step 1 and calculate the top product purity. Optimization is performed by changing the feed stage, the number and the location of the reactive trays, and the bottom flow rate. If the top purity is not 99% we run another simulation where the product purity is fixed at 99% and calculate the reflux ratio required to obtain it.

A.2.1.2 Very Fast Reaction Rate, Approach to Equilibrium, 3% Inert

The feed is 48.5% each isomer plus a 3% inert impurity (2,3-di-methyl-butadiene). The purge on the recycle stream, for both the designs, is now fixed at 5% based on the fresh feed. The simulation procedure is the same as in §A.2.1.1.

A.2.1.3 Very Fast Reaction Rate, Approach to Equilibrium, 20 Ideal Trays

The number of total ideal trays of both columns, reactive and non-reactive, is decreased to 20, the simulation procedure is the same as in §A.2.1.1.

A.2.1.4 Finite Reaction Rate, 95% Approach to Equilibrium at 58 ºC

The reaction rate is supposed to be finite and precisely it reaches 95% of the reaction equilibrium conversion at 58 °C.

To set a kinetic equation in Aspen Plus, an Arrhenius like equation, we need to define the activation energy and the pre-exponential coefficient for both the direct and the reverse reactions. In order to do that we use a relationship between the activation energies and the enthalpy of reaction[51]:

$$E_d - E_r = \Delta H_r \qquad \text{(a)}$$

The other relationship we use is that, at 58 °C, we assume the ratio between the direct and the reverse kinetic equations to be equal to 95% of the equilibrium conversion at the same temperature:

$$k_d \exp[-(E_d / RT)] / \; k_r \exp[-(E_r / RT)] = 0.95\ K_C \qquad \text{(b)}$$

In these two equations there are 4 unknowns (E_d, E_r, k_d, k_r), therefore we assume a reasonable value for E_r and k_r, and evaluate E_d and k_d. Once we obtain these 4 parameters, we use them in the Aspen Plus simulations.

To implement a kinetic equation in a reactive distillation column we need to define the volume of the tray. The tray volume is obtained, based on the internal column flow rates calculated in §A.2.1.1, following the procedure described in ref. 49.

In the reactive column, out of 40 total trays, we fix 20 reactive stages, therefore knowing the size of the single tray and the number of them we also know the total reactive volume. This last data is needed for the 2-unit design. In fact, since we have now a kinetic equation, we use a different reactor, a PFR where we fix the same kinetic parameters used in the catalytic column, and the reactor volume is equal to the total reactive volume of the column.

In the 2-unit scheme we fix the reflux ratio and the bottom flow rate as from §A.2.1.1 and calculate the top methyl acetate purity. If the purity does not meet the 99% purity specification we increase the PFR volume, independent of distillation, until we meet it.

In the reactive distillation column, the reflux ratio is the same as from §A.2.1.1, we calculate the top methyl acetate purity, optimizing the result manipulating the reaction region location and the feed stage. As usual, if 99% purity is not reached, we fix 99% top purity and we calculate the reflux ratio needed to reach it.

A.2.1.5 Finite Reaction Rate, Very Slow Reaction Rate

We change the kinetic parameters in order to obtain slower reaction rates as compared to §A.2.1.4. The procedure of the simulation is then the same as in §A.2.1.1.

A.2.1.6 Impact of Flow Mal-Distribution, Finite Reaction Rate, 95% Approach to Equilibrium at 58 °C

The only difference between this example and the one in §A.2.1.4 is that to take in consideration a lower separation and reaction efficiency, in the catalytic column, due to flow mal-distribution, we lower the total number of ideal trays from 40 to 30, out of which 15 are reactive. The non-reactive distillation column does not change, as there is no catalyst. The rest of the procedure is the same as in §A.2.1.4.

A.2.2 Production of normal-Hexane, Very fast Reaction Rate, Approach to Equilibrium

The main product, separated from the bottom, is normal-hexane, required to reach 99% purity. The temperature of the external CSTR, independent of distillation requirements, is 250 °C, operated at 40 atm. The rest of the procedure is the same as in §A.2.1.1.

A.2.3 Production of cyclo-Hexane, Very fast Reaction Rate, Approach to Equilibrium

In this example we consider the isomerization between cyclo-hexane and methyl-cyclo-pentane. The main product is cyclo-hexane, separated from the bottom at 99% purity, the temperature of the external CSTR, independent of distillation requirements, is 50 °C, operated at 1 atm. The rest of the procedure is the same as in §A.2.1.1.

A.2.4 Production of Methyl-cyclo-Pentane, Very fast Reaction Rate, Approach to Equilibrium

The main product is methyl-cyclo-pentane, separated from the top at 99% purity, the temperature of the external CSTR, independent of distillation requirements, is 300 °C, operated at 30 atm. The rest of the procedure is the same as in §A.2.1.1.

A.2.5 Production of 2,3-di-Methyl-Butane, Very fast Reaction Rate, Approach to Equilibrium. Retrofit of an Existing Non-Reactive Column

In this example we start with a non-reactive “RadFrac” distillation column, with 40 ideal trays. The feed is a 50/50 mixture of the two isomers (5 kmol/hr each, 2-3-di-methyl-butane and normal-hexane). The main product is distilled from the top.

In the first step, we fix the distillate flow rate at 5 kmol/hr, and the top methyl acetate purity is required to be 99%. The manipulated variable to reach the product specification is the reflux ratio, the result of the simulation, while the feed stage is changed for optimization purposes.

In the second step, we take the same column, and fix 20 reactive trays, with a very slow reaction rate; the kinetic parameters are evaluated as in §A.2.1.5. The reflux ratio is the same as from the first step, and the product specification is again 99% methyl acetate top purity. This time the manipulated variable is the distillation flow rate, the result of the simulation. The feed stage and the reactive region location are changed for optimization.

Pure components	T at 1 atm (°C)	T at 10 atm (°C)
Methyl Acetate	57.1	143.6
Methanol	64.5	137.3
Water	100.0	180.5
Acetic Acid	117.9	213.1
Sulfuric Acid	274.8	344.6
Azeotropes		
Methyl Acetate-Methanol	53.9	130.2
Methyl Acetate-Water	56.1	139.5

Table 1. Effect of Pressure on the Boiling Points.
(Methyl Acetate Production)

Items	**Requirements and Limitations**
Reaction and Distillation Temperature	Common Temperature Range.
Solid Catalysts	Active in the Same Common Temperature Range with Low Deactivation Rate.
Flow Distribution Inside Catalytic Trays or Packings	Good Flow Pattern Required for High Reaction Conversion.
Space Velocity	Determined by Distillation, Unavailable to Be Adjusted for Reaction.

Table 2. Limitations of Reactive Distillation with Solid Catalysts Inside a Column.

(Methyl Acetate Production)

Remedy	**Product Purity (%)**	**RR**
None	**97.8**	**2.2**
Liquid Flow Rate Circulated from the Column to the External Reactors 6 Times the Internal Liquid Down-Stream	**99.0**	**2.1 – 2.5**
Liquid Flow Rate Circulated from the Column to the External Reactors 3 Times the Internal Liquid Down-Stream and 5% AA Excess in the Feed	**99.0**	**2.1 – 2.5**
Manipulation of Temperature in the Side-Reactors	**99.0**	**2.1 – 2.5**

Table 3. Methyl Acetate Purity in the Top Distillate Product

In a 60 Tray Non-Reactive Distillation Column with 4 Side-Reactors When Several Remedies Are Applied.

(Methyl Acetate Production).

Output	Manipulated Parameters		
Product Purity (%)	Reactive Trays	Location	Feed Tray*
95.7	1	21st	21st
97.6	1	31st	31st
98.1	1	36th	36th
98.4	1	40th	40th
95.7	5	21st-25th	25th
96.8	5	26th-30th	30th
97.6	5	31st-35th	35th
98.1	5	36th-40th	40th
95.7	10	21st-30th	30th
96.8	10	26th-35th	35th
97.6	10	31st-40th	40th
90.7	20	11th-30th	30th
93.9	20	16th-35th	35th
95.7	20	21st-40th	40th

Table 4. Optimum Placement of Fresh Feed and Reactive Trays.

40-Trays Reactive Column with Very Fast Catalyst, Approach to Equilibrium.

(n-Hexane to 2,3-di-Methyl-Butane Isomerization)

(Highlighted are the best results)

Desired Product: 2,3-di-Methyl-Butane

Feed: n-Hexane = 5 kmol/hr
2,3-di-Methyl-Butane = 5 kmol/hr
P = 1 atm
Purge is set to 0.
Recycle: Bottom stream
Recycle/Fresh Feed = 0.9
Vapor/Fresh Feed = 5.2
Recycle/Fresh Feed and Vapor/Fresh Feed are the best results for the reactor + distillation column configuration (Table 5).
*: if the feed tray is one of the reactive trays or it is located below the reactive region, the results do not change.

Step	**Design**	**Reactor Temp. (^oC)**	**Recycle/ Fresh Feed**	**Vapor/ Fresh Feed**	**Product Purity (%)**	**Reactive Trays**	**Location**	**Feed Tray**
I	R+C	58	**0.9**	**5.2**	99.0	**---**	**---**	***30th***
I	R+C	38	**0.8**	**5.0**	99.0	**---**	**---**	***31st***
II	RD	---	0	5.2	**98.4**	***1***	***40th***	***40th***
II	RD	---	0	**5.8**	99.0	***1***	***40th***	***40th***

Table 5. Comparison between Two-Unit Scheme and Reactive Distillation Column.

Reaction with Very Fast Catalyst, Approach to Equilibrium.

(n-Hexane to 2,3-di-Methyl-Butane Isomerization)

(R+C: External Reactor + Conventional Distillation Column.
RD: Reactive Distillation Column.)

Desired Product: 2,3-di-Methyl-Butane

Feed: n-Hexane = 5 kmol/hr
2,3-di-Methyl-Butane = 5 kmol/hr
Recycle: Bottom Stream
P = 1 atm
Purge is set to 0.
40 total trays for both, reactive and non-reactive, columns.

The results of the simulations and in bold
The manipulated parameters in the simulations are in bold and italic
The values in normal font are inputs to the simulations

Step	**Design**	**Catalyst (Kg)**	**Recycle/ Fresh Feed**	**Vapor/ Fresh Feed**	**Product Purity (%)**	**Reactive Trays**	**Location**	**Feed Tray**
I	R+C	1000	0.9	5.2	**98.6**	---	***---***	***30th***
I	R+C	***1300***	0.9	5.2	99.0	---	***---***	***30th***
II	RD	1000*	0	5.2	**98.2**	20	***21st-40th***	***37th***
II	RD	1000	0	**6.1**	99.0	20	***21st-40th***	***37th***

Table 6. **Comparison between Two-Unit Scheme and Reactive Distillation Column.**

Reaction with Finite Reaction Rate, 95% Approach to Equilibrium at 58 ºC.

(n-Hexane to 2,3-di-Methyl-Butane Isomerization).

(R+C: External Reactor + Conventional Distillation Column.
RD: Reactive Distillation Column.)

Desired Product: 2,3-di-Methyl-Butane

Feed: n-Hexane = 5 kmol/hr
2,3-di-Methyl-Butane = 5 kmol/hr
Recycle: bottom stream
P = 1 atm
Purge is set to 0.
40 total trays.
The external reactor is operated at 58 °C.

The results of the simulations and in bold
The manipulated parameters in the simulations are in bold and italic
The values in normal font are inputs to the simulations

*: It comes from column dimension.

Case	Design	Catalyst (Kg)	Catalyst Activity* (1/hr)	Recycle/ Fresh Feed	Vapor/ Fresh Feed	Product Purity (%)	Reactive Trays	Location	Feed Tray
I	R+C	***1300***	***0.662***	0.9	5.2	99.0	---	**---**	***30th***
	RD	1000	0.662	0	5.2	**98.2**	20	***21st-40th***	***37th***
	RD	1000	0.662	0	**6.1**	99.0	20	***21st-40th***	***37th***
II	R+C	***3000***	***0.287***	0.9	5.2	99.0	---	**---**	***30th***
	RD	1000	0.287	0	5.2	**97.2**	20	***21st-40th***	***33rd***
	RD	1000	0.287	0	**6.6**	99.0	20	***21st-40th***	***33rd***
III	R+C	***5000***	***0.172***	0.9	5.2	99.0	---	**---**	***30th***
	RD	1000	0.172	0	5.2	**92.0**	20	***21st-40th***	***25th***
	RD	1000	0.172	0	**9.0**	99.0	20	***21st-40th***	***25th***
IV	R+C	***10000***	***0.086***	0.9	5.2	99.0	---	**---**	***30th***
	RD	1000	0.086	0	5.2	**83.8**	20	***21st-40th***	***11th***
	RD	1000	0.086	0	**625**	99.0	20	***21st-40th***	***16th***

Table 7. Comparison between Two-Unit Scheme and Reactive Distillation Column.

Reaction with Finite Reaction Rate, Very Slow Catalyst.

(n-Hexane to 2,3-di-Methyl-Butane Isomerization).

(R+C: External Reactor + Conventional Distillation Column.
RD: Reactive Distillation Column.)

Space Velocity Is Lowered to Consider a Very Slow Catalyst, but It Can Also Simulate Catalyst Aging or Deactivation.

Desired Product: 2,3-di-Methyl-Butane

Feed: 10 kmol/hr = 860 kg/hr
n-Hexane = 5 kmol/hr
2,3-di-Methyl-Butane = 5 kmol/hr
*: Mass Feed Flow Rate/Mass of Catalyst Used to Convert It
Recycle: bottom stream
P = 1 atm
Purge is set to 0.
40 total trays.
The external reactor is operated at 58 °C.

The results of the simulations and in bold
The manipulated parameters in the simulations are in bold and italic
The values in normal font are inputs to the simulations

Step	Design	Reactor Temp. (ºC)	Recycle/ Fresh Feed	Vapor/ Fresh Feed	Product Purity (%)	Reactive Trays	Location	Feed Tray
I	R+C	58	**1.6**	**7.9**	99.0	**---**	**---**	***30th***
I	R+C	38	**1.2**	**7.6**	99.0	**---**	**---**	***29th***
II	RD	---	0	8.1	**99.3**	***10***	***31st-40th***	***31st***
II	RD	---	0	**7.3**	99.0	***10***	***31st-40th***	***31st***

Table 8. Comparison between Two-Unit Scheme and Reactive Distillation Column.

Reaction with Very Fast Catalyst, Approach to Equilibrium, and 3% Inert Impurity in the Feed.

(n-Hexane to 2,3-di-Methyl-Butane Isomerization).

(R+C: External Reactor + Conventional Distillation Column.
RD: Reactive Distillation Column.)

Desired Product: 2,3-di-Methyl-Butane

Feed: n-Hexane = 4.85 kmol/hr
2,3-di-Methyl-Butane = 4.85 kmol/hr
Inert (2,3-di-methyl-butadiene) = 0.3 kmol/hr
Recycle: bottom stream
P = 1 atm
Purge: 5% of Fresh Feed
40 total trays.

The results of the simulations and in bold
The manipulated parameters in the simulations are in bold and italic
The values in normal font are inputs to the simulations

Step	**Design**	**Reactor Temp. (°C)**	**Recycle (kmol/hr)**	**Vapor/ Fresh Feed**	**Product Purity (%)**	**Reactive Trays**	**Location**	**Feed Tray**
I	R+C	58	**3.0**	**8.4**	99.0	**---**	**---**	***18th***
I	R+C	38	**2.6**	**8.0**	99.0	**---**	**---**	***17th***
II	RD	---	0	8.4	**98.9**	***1***	***20th***	***20th***
II	RD	---	0	**8.6**	99.0	***1***	***20th***	***20th***

Table 9. **Comparison between Two-Unit Scheme and Reactive Distillation Column.**

Reaction with Very Fast Catalyst, Approach to Equilibrium.

(n-Hexane to 2,3-di-Methyl-Butane Isomerization).

20 Total Trays for both, Reactive and Non-Reactive, Columns

(R+C: External Reactor + Conventional Distillation Column.
RD: Reactive Distillation Column.)

Desired Product: 2,3-di-Methyl-Butane

Feed: n-Hexane = 5 kmol/hr
2,3-di-Methyl-Butane = 5 kmol/hr
Recycle: bottom stream
P = 1 atm
Purge is set to 0.

The results of the simulations and in bold
The manipulated parameters in the simulations are in bold and italic
The values in normal font are inputs to the simulations

Step	Design	Ideal Trays	Catalyst (Kg)	Recycle/ Fresh Feed	Vapor/ Fresh Feed	Product Purity (%)	Reactive Trays	Location	Feed Tray
I	R+C	40	***1300***	**0.9**	**5.2**	99.0	---	**---**	**30th**
II	RD	30	750	0	5.2	**94.6**	15	**16th-30th**	**22nd**
II	RD	30	750	0	**9.4**	99.0	15	**16th-30th**	**22nd**

Table 10. Impact of Flow Mal-distribution Due to Heterogeneous Catalysts.

Comparison between Two-Unit Scheme and Reactive Distillation Column.

Reaction with Finite Reaction Rate, 95% Approach to Equilibrium at 58 °C.

(n-Hexane to 2,3-di-Methyl-Butane Isomerization).

Reactive Column: 30 Ideal Trays (to account for lower efficiency).
Non-Reactive Column: 40 Ideal Trays.

(R+C: External Reactor + Conventional Distillation Column.
RD: Reactive Distillation Column.)

Desired Product: 2,3-di-Methyl-Butane

Feed: n-Hexane = 5 kmol/hr
2,3-di-Methyl-Butane = 5 kmol/hr
Recycle: bottom stream
P = 1 atm
Purge is set to 0.
The external reactor is operated at 58 °C.

The results of the simulations and in bold
The manipulated parameters in the simulations are in bold and italic
The values in normal font are inputs to the simulations

Step	**Design**	**Reactor Temp. (°C)**	**Recycle/ Fresh Feed**	**Vapor/ Fresh Feed**	**Product Purity (%)**	**Reactive Trays**	**Location**	**Feed Tray**
I	R+C	250	**1.2**	**5.8**	99.0	**---**	**---**	***15th***
II	RD	---	1.2	5.8	**82.3**	***1***	***2nd***	***2nd***
II	RD	---	1.2	**8.3**	99.0	***1***	***2nd***	***2nd***

Table 11. **Comparison between Two-Unit Scheme and Reactive Distillation Column.**

Reaction with Very Fast Catalyst, Approach to Equilibrium.

(2,3-di-Methyl-Butane to n-Hexane Isomerization).

(R+C: External Reactor + Conventional Distillation Column.
RD: Reactive Distillation Column.)

Desired Product: n-Hexane

Feed: n-Hexane = 5 kmol/hr
2,3-di-Methyl-Butane = 5 kmol/hr
Recycle: top stream
P = 1 atm the two columns, and 40 atm the reactor.
Purge is set to 0.
40 total trays.

The results of the simulations and in bold
The manipulated parameters in the simulations are in bold and italic
The values in normal font are inputs to the simulations

Step	Design	Reactor Temp. (ºC)	Recycle/ Fresh Feed	Vapor/ Fresh Feed	Product Purity (%)	Reactive Trays	Location	Feed Tray
I	R+C	50	**2.0**	**4.4**	99.0	**---**	**---**	***5th***
II	RD	---	2.0	4.4	**98.7**	***1***	***2nd***	***2nd***
II	RD	---	2.0	**4.7**	99.0	***1***	***2nd***	***2nd***

Table 12. **Comparison between Two-Unit Scheme and Reactive Distillation Column.**

Reaction with Very Fast Catalyst, Approach to Equilibrium.

(Methyl-cyclo-Pentane to cyclo-Hexane Isomerization).

(R+C: External Reactor + Conventional Distillation Column.
RD: Reactive Distillation Column.)

Desired Product: cyclo-Hexane

Feed: cyclo-Hexane = 5 kmol/hr (81.4 C)
Methyl-cyclo-Pentane = 5 kmol/hr (71.5 C)
Recycle: top stream
P = 1 atm
Purge is set to 0.
40 total trays.

The results of the simulations and in bold
The manipulated parameters in the simulations are in bold and italic
The values in normal font are inputs to the simulations

Step	Design	Reactor Temp. (°C)	Recycle/ Fresh Feed	Vapor/ Fresh Feed	Product Purity (%)	Reactive Trays	Location	Feed Tray
I	R+C	300	**1.7**	**4.8**	99.0	***---***	***---***	***34th***
II	RD	---	0	4.8	**56.2**	***1***	***40th***	***40th***
II	RD	---	0	**12.6**	99.0	***1***	***40th***	***40th***

Table 13. Comparison between Two-Unit Scheme and Reactive Distillation Column.

Reaction with Very Fast Catalyst, Approach to Equilibrium.

(cyclo-Hexane to Methyl-cyclo-Pentane Isomerization).

(R+C: External Reactor + Conventional Distillation Column.
RD: Reactive Distillation Column.)

Desired Product: Methyl-cyclo-Pentane

Feed: cyclo-Hexane = 5 kmol/hr (81.4 C)

Methyl-cyclo-Pentane = 5 kmol/hr (71.5 C)
Recycle: bottom stream
P = 1 atm the two columns, and 30 atm the reactor.
Purge is set to 0.
40 total trays.

The results of the simulations and in bold
The manipulated parameters in the simulations are in bold and italic
The values in normal font are inputs to the simulations

Distillate Flow Rate (kmol/hr)	**Product Purity (%)**	**Vapor/ Fresh Feed**	**Feed Tray**
5 (50% of the Feed)	99.0	**14.4**	***21st***

Table 14a. Non-Reactive Distillation Column to Separate 2,3-di-Methyl-Butane from n-Hexane.

Catalyst (Kg)	**Distillate (kmol/hr)**	**Increased Productivity (%)**	**Vapor/ Fresh Feed**	**Product Purity (%)**	**Reactive Trays**	**Location**	**Feed Tray**
1000	**8.7** (87% of the Feed)	**73.3**	14.4	99.0	20	***21st-40th***	***21st***

Table 14b. Same Column as in Table 14a with Very Slow Catalyst Filled in It. (The Catalyst Is the Same as in Step IV of Table 7)

(n-Hexane to 2,3-di-Methyl-Butane Isomerization)

Desired Product: 2,3-di-Methyl-Butane

Feed: n-Hexane = 5 kmol/hr
2,3-di-Methyl-Butane = 5 kmol/hr
Recycle: bottom stream
P = 1 atm
Purge is set to 0.
40 total trays.

The results of the simulations and in bold
The manipulated parameters in the simulations are in bold and italic
The values in normal font are inputs to the simulations

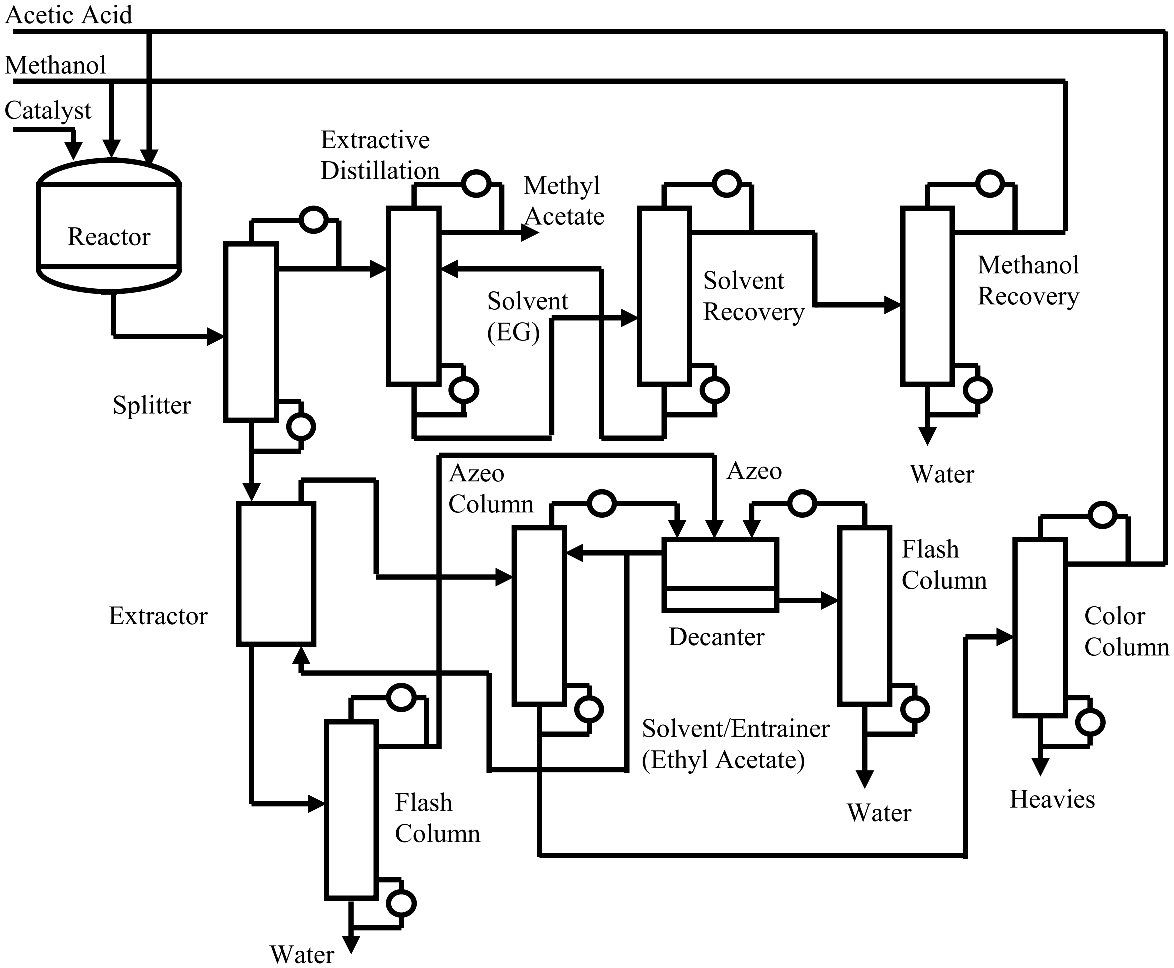


Figure 1. Conventional Scheme to Produce Methyl Acetate.

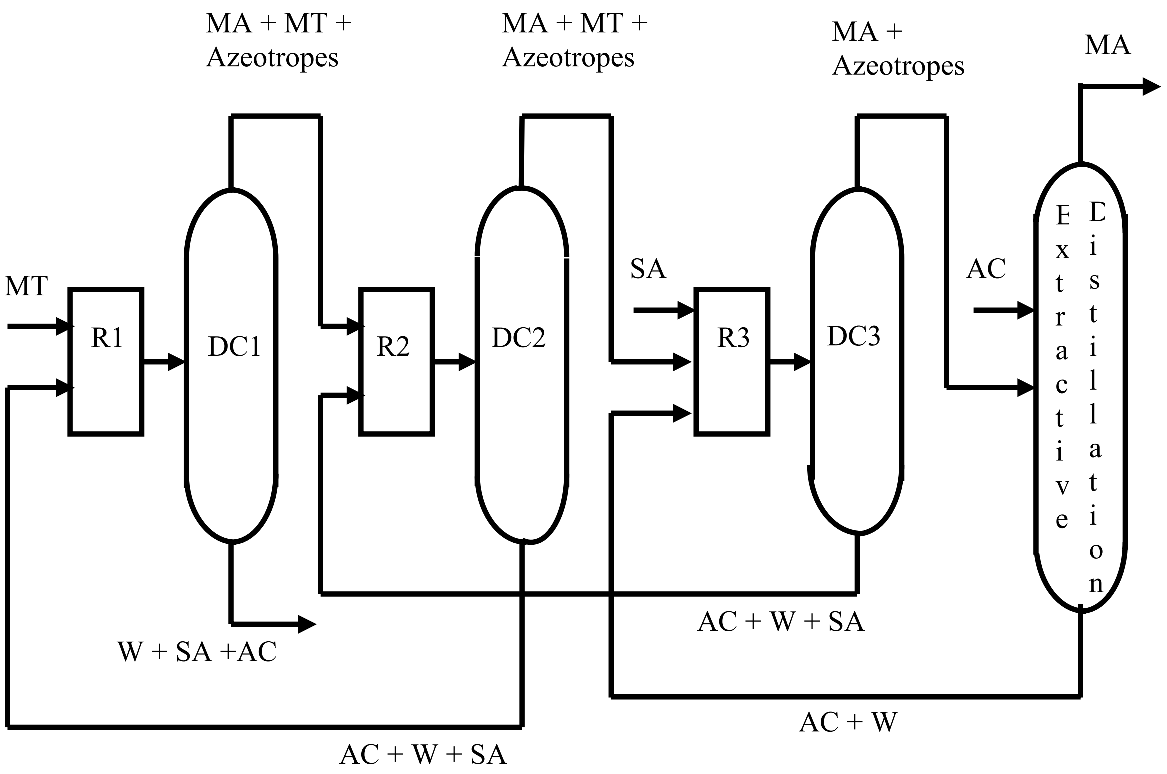


Figure 2. **Countercurrent Reactor Train with Separation in Between. (Methyl Acetate Production).**

(R = Reactor; DC = Non-Reactive Distillation Column; MA = Methyl Acetate; AC = Acetic Acid; MT = Methanol; W = Water; SA = Sulfuric Acid).

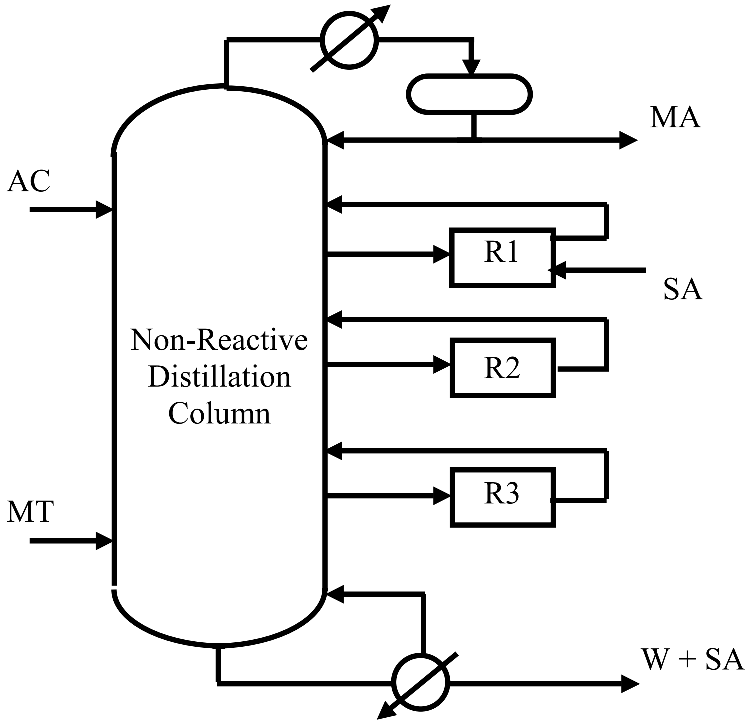


Figure 3. **Side-Reactors Cascaded into a Non-Reactive Distillation Column. (Methyl Acetate Production).**

(R = Reactor; MA = Methyl Acetate; AC = Acetic Acid; MT = Methanol; W = Water; SA = Sulfuric Acid).

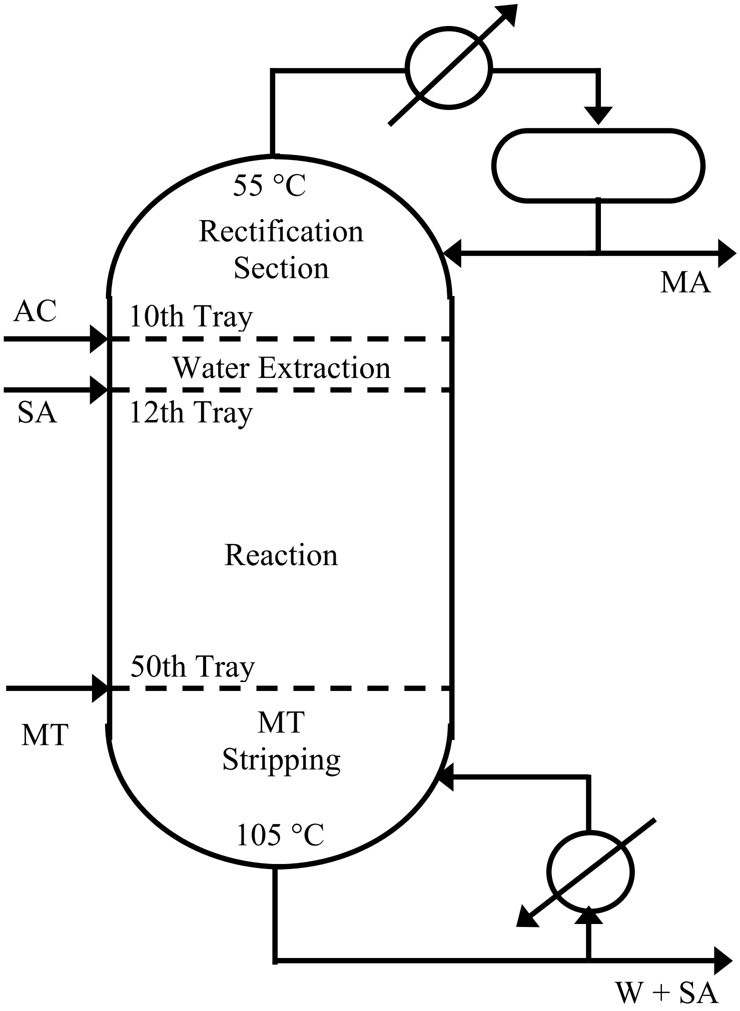


Figure 4. **Reactive Distillation Column.**

(Methyl Acetate Production).

Trays 1-9:	Rectification Section MA separated from AC.
Trays 10-11:	Extractive Distillation Section W extracted by AC.
Trays 12-50:	Countercurrent Reaction Region MT reacts with AC
Trays 51-60:	Stripping Section MT stripped from by-product W (reaction also takes place).

(MA = Methyl Acetate; AC = Acetic Acid; MT = Methanol; W = Water; SA = Sulfuric Acid).

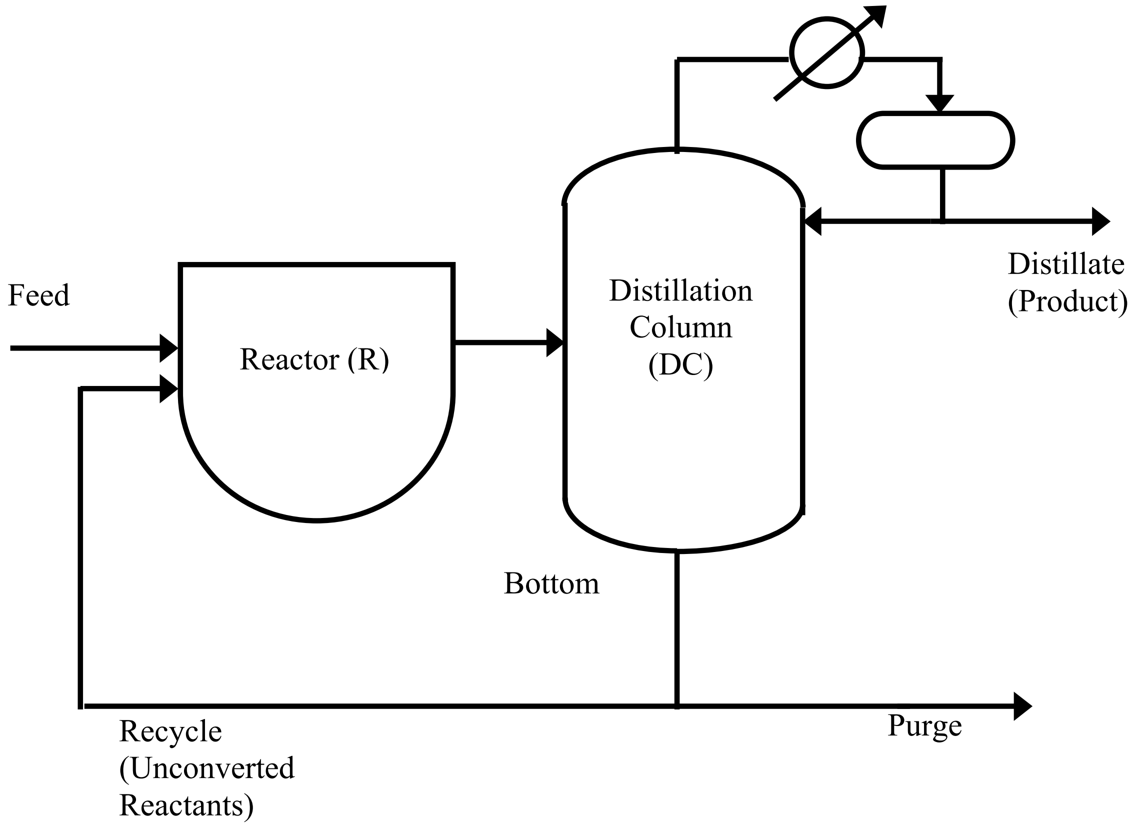


Figure 5. **Reactor with Recycle from a Distillation Column for Reactive Systems with Equilibrium Limitations.**

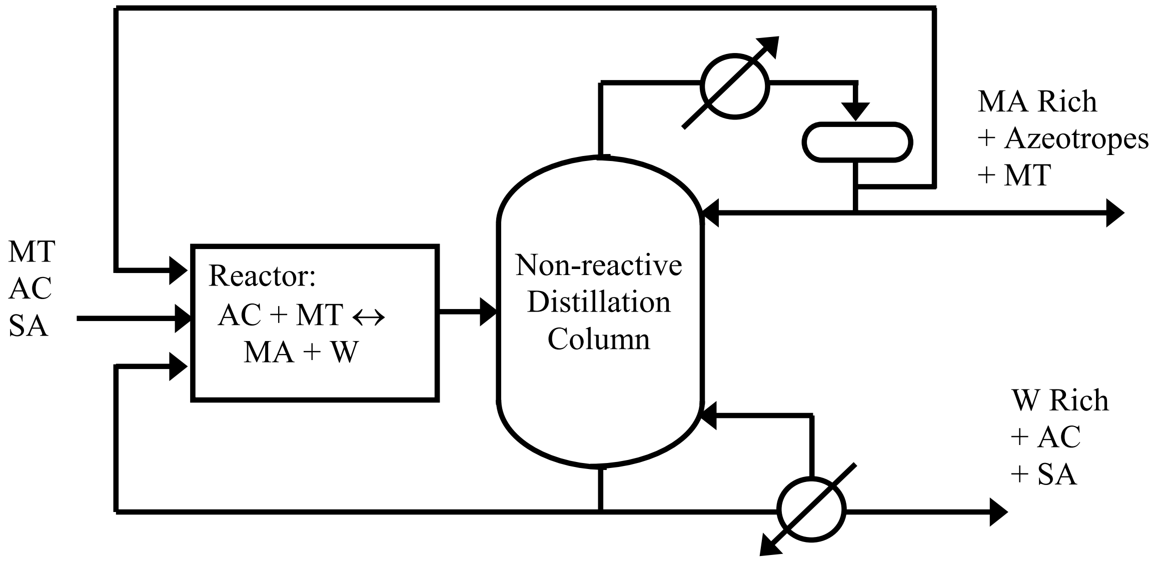


Figure 6. **Conventional Scheme with a Rector Followed by a Non-Reactive Distillation Column.**

(Methyl Acetate Production).

(MA = Methyl Acetate; AC = Acetic Acid; MT = Methanol; W = Water; SA = Sulfuric Acid).

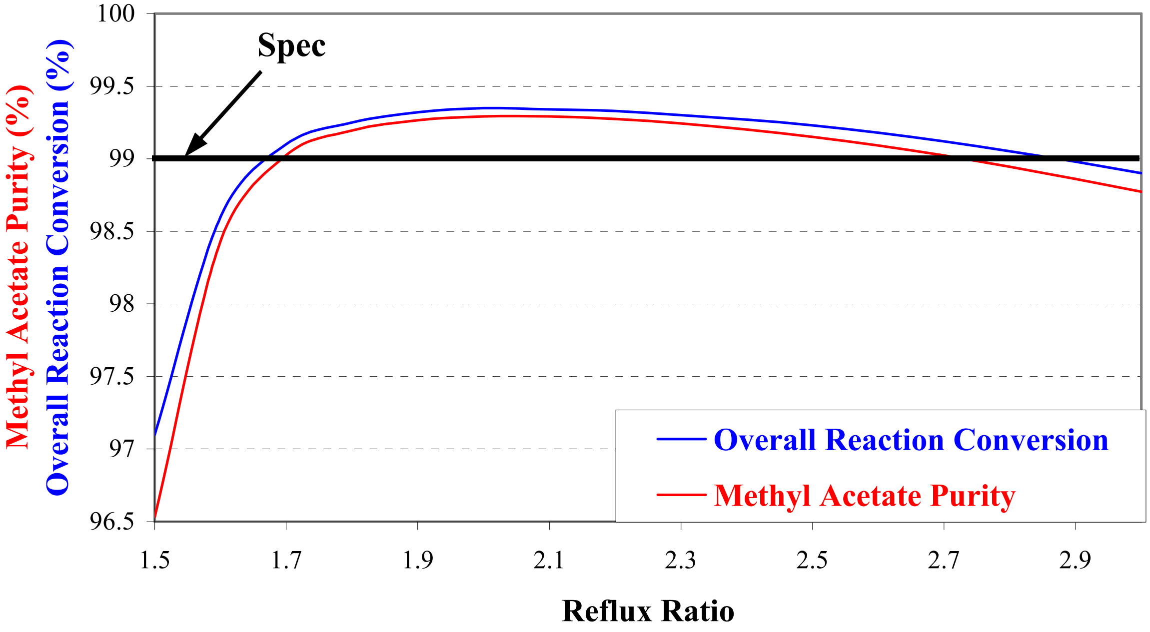


Figure 7. **Methyl Acetate Purity in the Distillate and Overall Reaction Conversion *Vs* Reflux Ratio.**

(Methyl Acetate Production).

(Spec: 99% methyl acetate purity in the top distillate product;
Reflux Ratio: Liquid Down Flow/Distillate Flow Rate;
60 total trays column, with 49 reactive trays from 12 to 60;
MT fed at stage 10; AC fed at stage 50; MA is the top distillate)

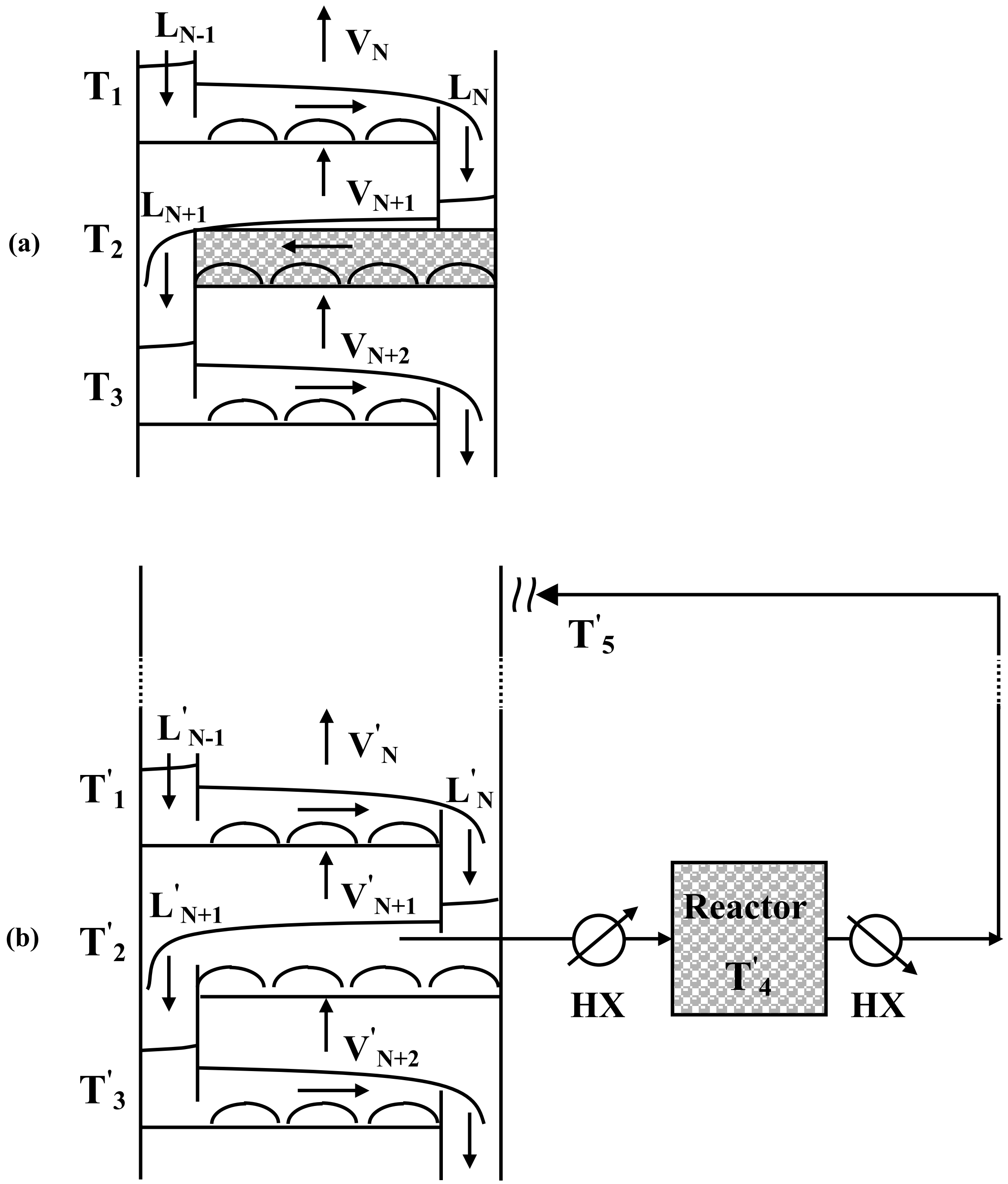


Figure 8. **Schematics of:**

(a) Conventional Reactive Tray.

(b) External Reactor.

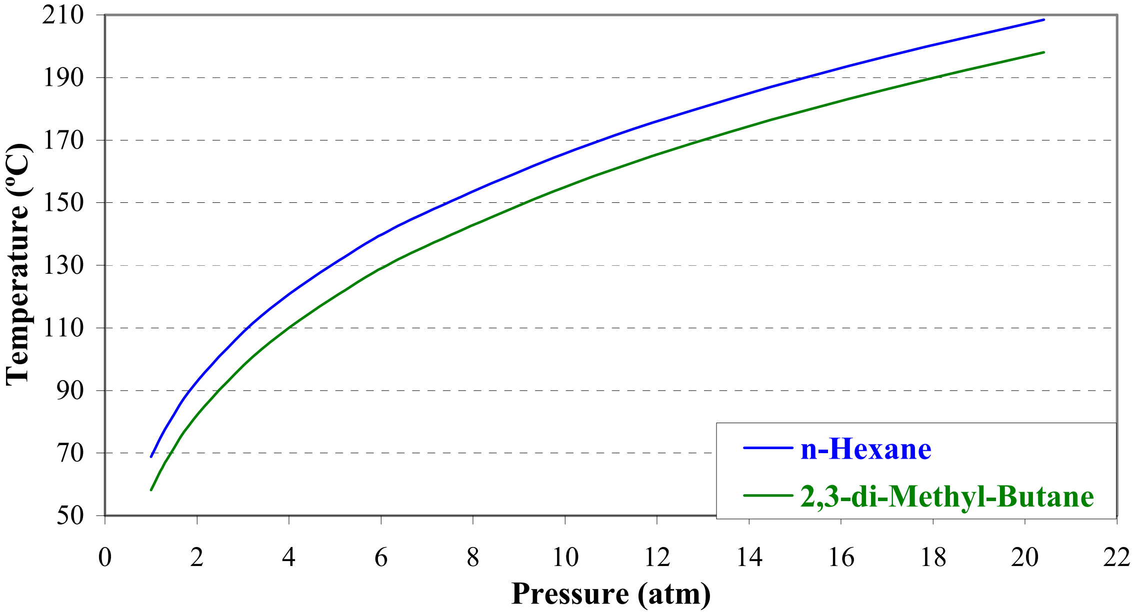


Figure 9. Boiling Point of n-Hexane and 2,3-di-Methyl-Butane *Vs* Pressure.

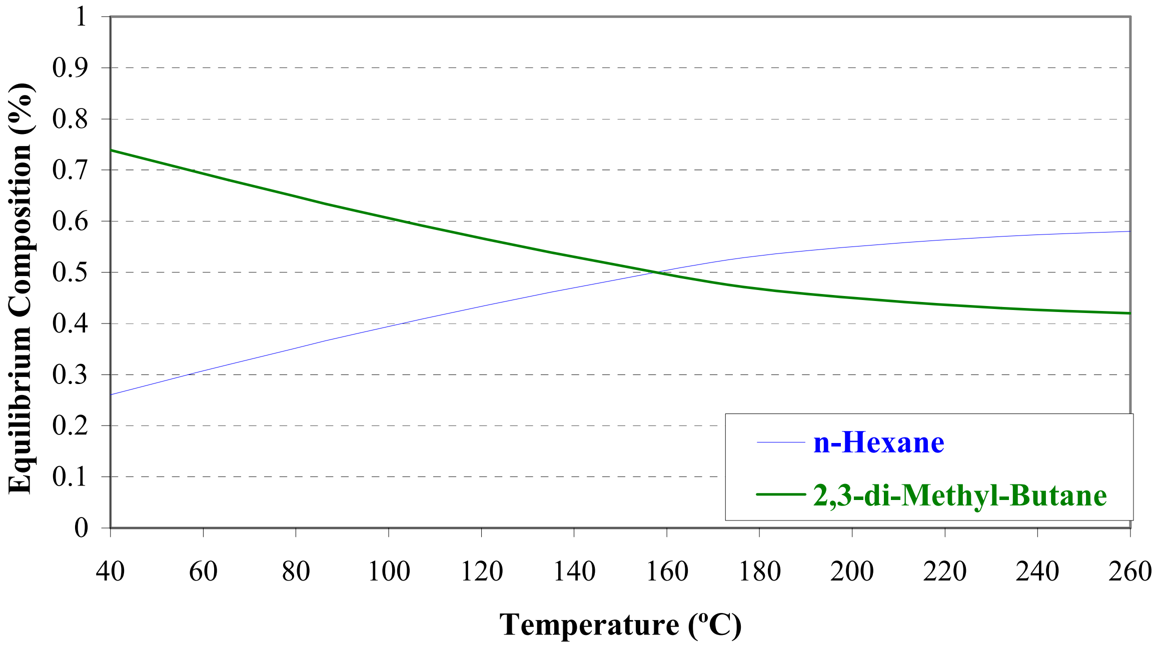


Figure 10. **n-Hexane and 2,3-di-Methyl-Butane Reaction Equilibrium Composition *Vs* Temperature.**

(Pressure has no impact)

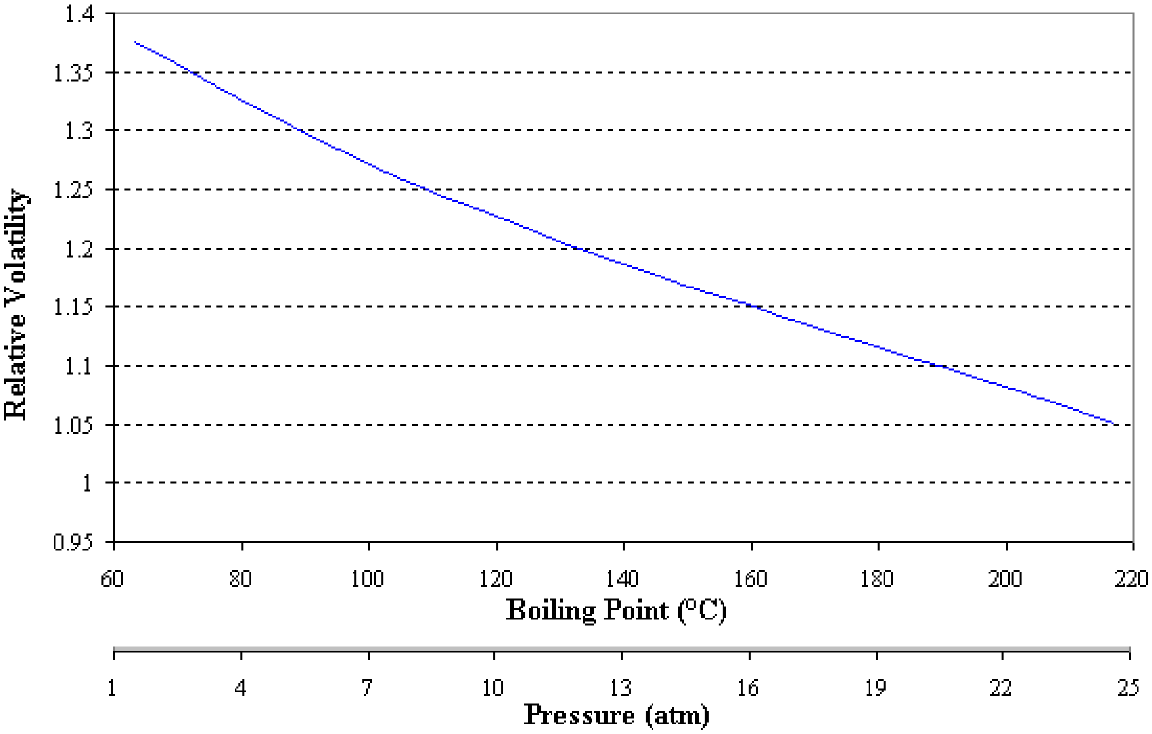


Figure 11. **2,3-diMB/n-H Relative Volatility *Vs* Boiling Point of a 50/50 Mixture of the Two Isomers at Different Pressures.**

(2,3-diMB = 2,3-di-Methyl-Butane; n-H = n-Hexane)

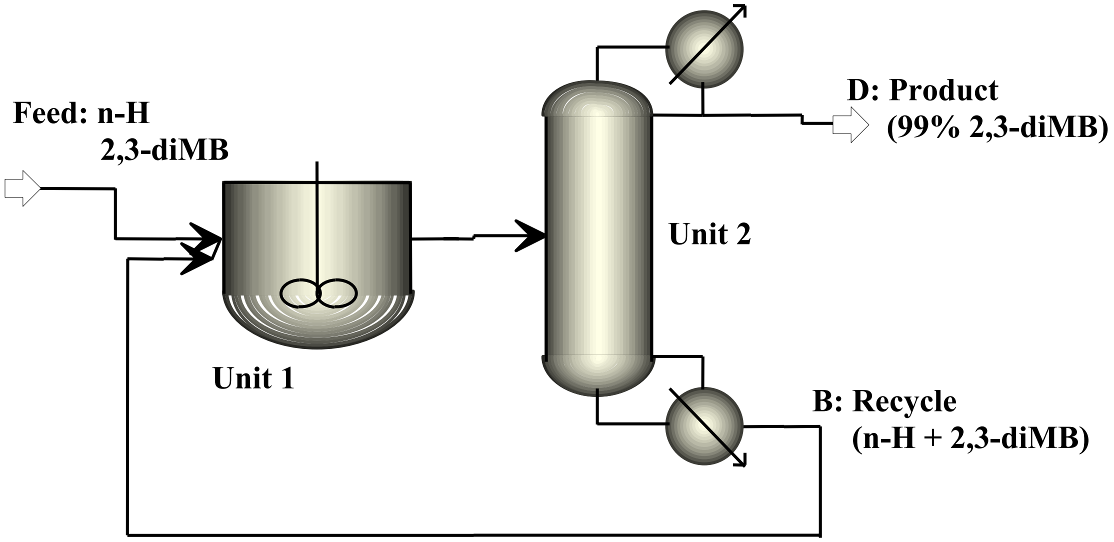


Figure 12. Reactor (Unit 1) + Non-Reactive Distillation Column (Unit 2).

(n-H to 2,3-diMB Isomerization).

Desired Product: 2,3-diMB

(2,3-diMB = 2,3-di-Methyl-Butane; n-H = n-Hexane;
D = Distillate Flow Rate; B = Bottom Flow Rate).

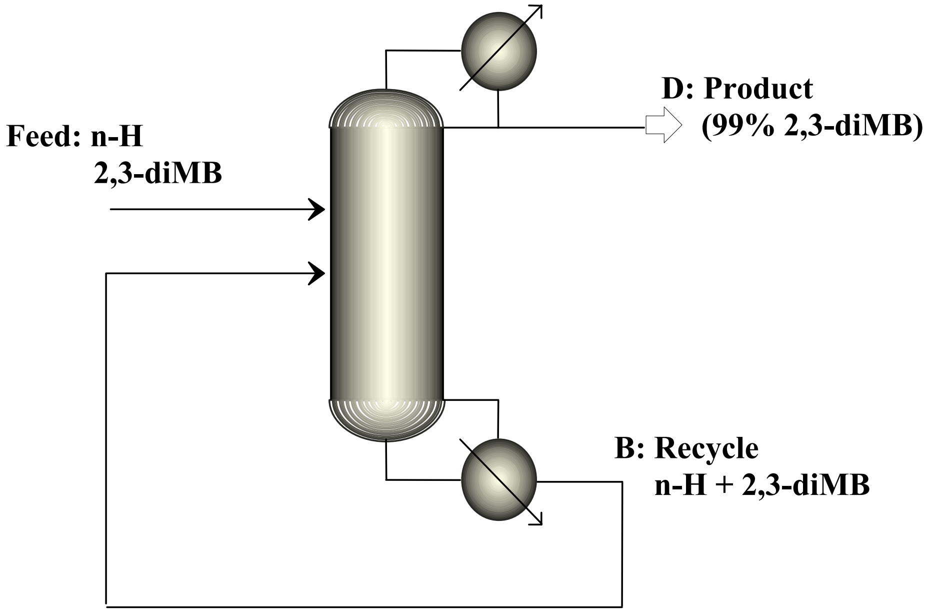


Figure 13. Reactive Distillation Column.

(n-H to 2,3-diMB Isomerization).

Desired Product: 2,3-diMB

(2,3-diMB = 2,3-di-Methyl-Butane; n-H = n-Hexane;
D = Distillate Flow Rate; B = Bottom Flow Rate).

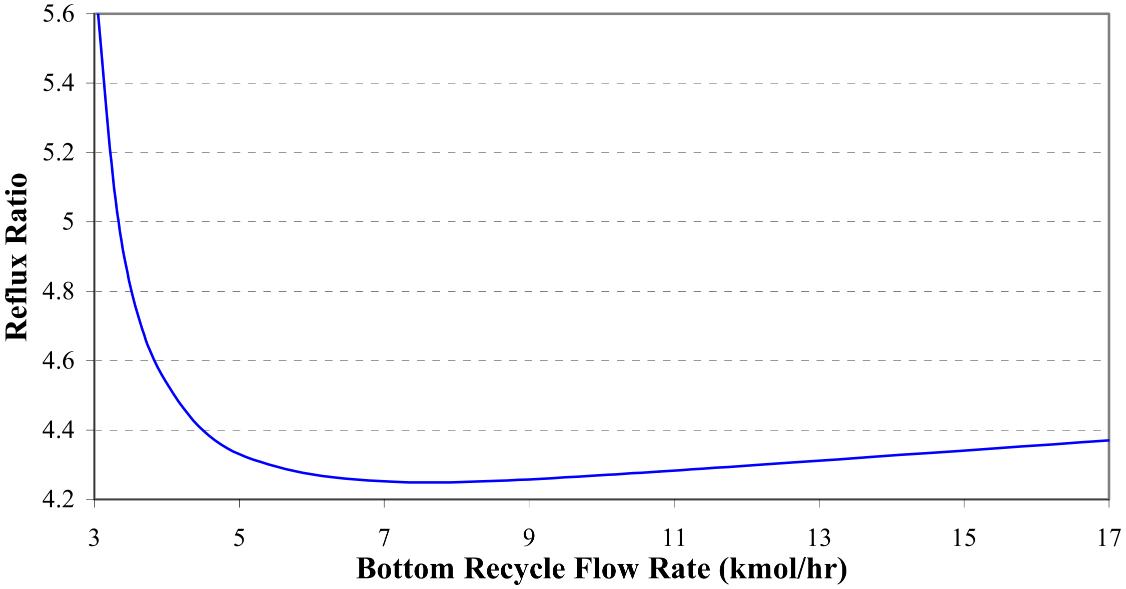


Figure 14. **Reflux Ratio *Vs* Bottom Recycle Flow Rate for the Two-Unit Scheme. Reaction with Very Fast Catalyst, Approach to Equilibrium. (n-H to 2,3-diMB Isomerization). Desired Product: 2,3-diMB**

(Reflux Ratio: Liquid Down Flow/Distillate Flow Rate;
2,3-diMB = 2,3-di-Methyl-Butane; n-H = n-Hexane;
Reactor + 40-Trays Non-Reactive Distillation Column scheme -the feed tray is the 30th from the top;
Feed: 10 kmol/hr, 50% each isomer)

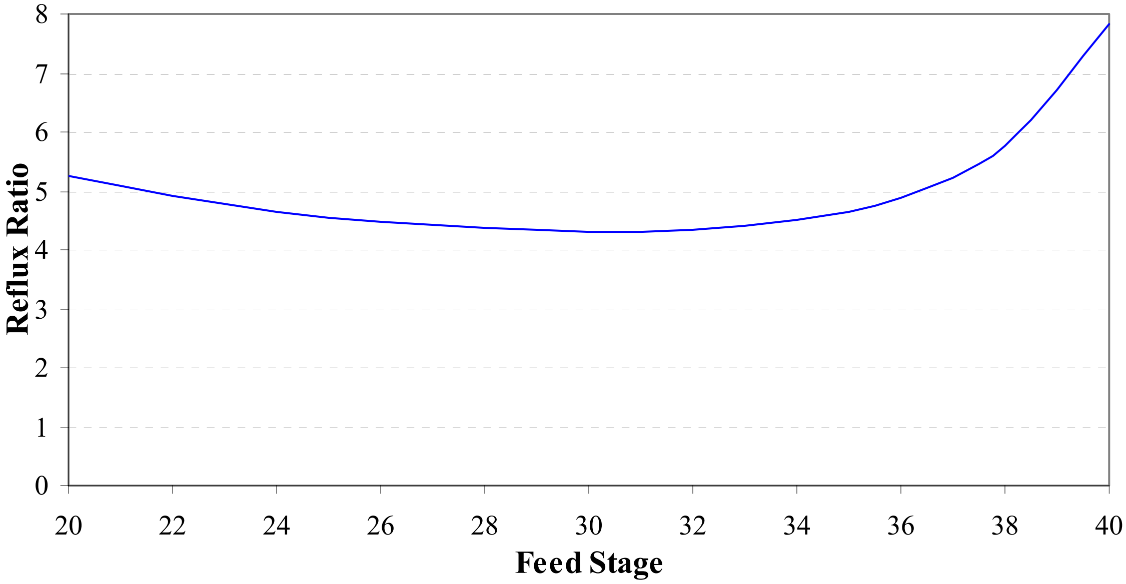


Figure 15. **Reflux Ratio *Vs* Feed Stage for the Two-Unit Scheme.**

Reaction with Very Fast Catalyst, Approach to Equilibrium.

(n-H to 2,3-diMB Isomerization).

Desired Product: 2,3-diMB

(Reflux Ratio: Liquid Down Flow/Distillate Flow Rate;
2,3-diMB = 2,3-di-Methyl-Butane; n-H = n-Hexane;
Reactor + 40-Trays Non-Reactive Distillation Column scheme -B is fixed at 8.7 kmol/hr;
Feed: 10 kmol/hr, 50% each isomer)

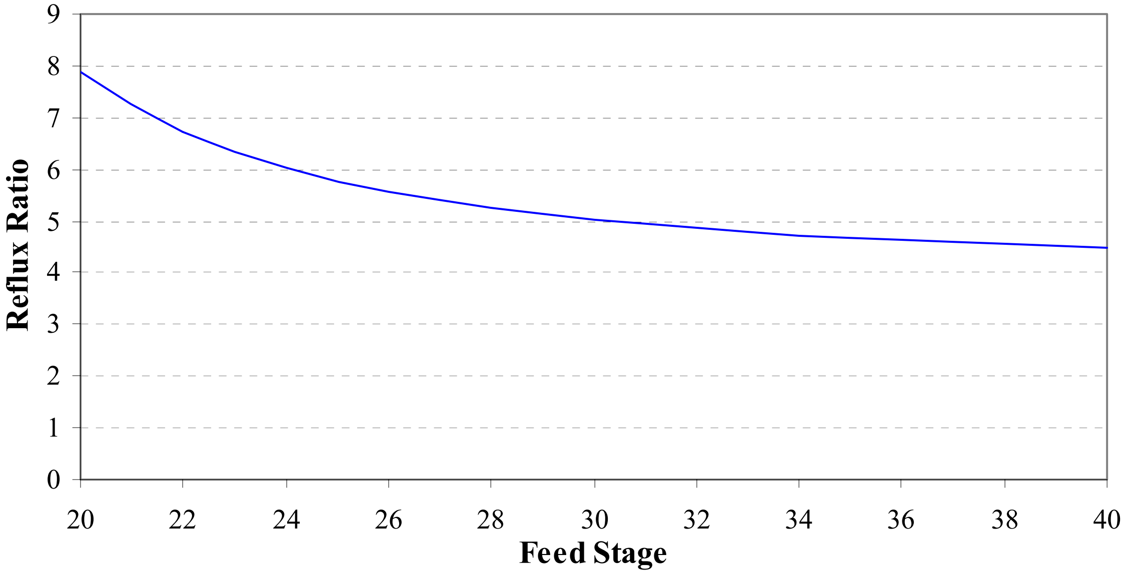
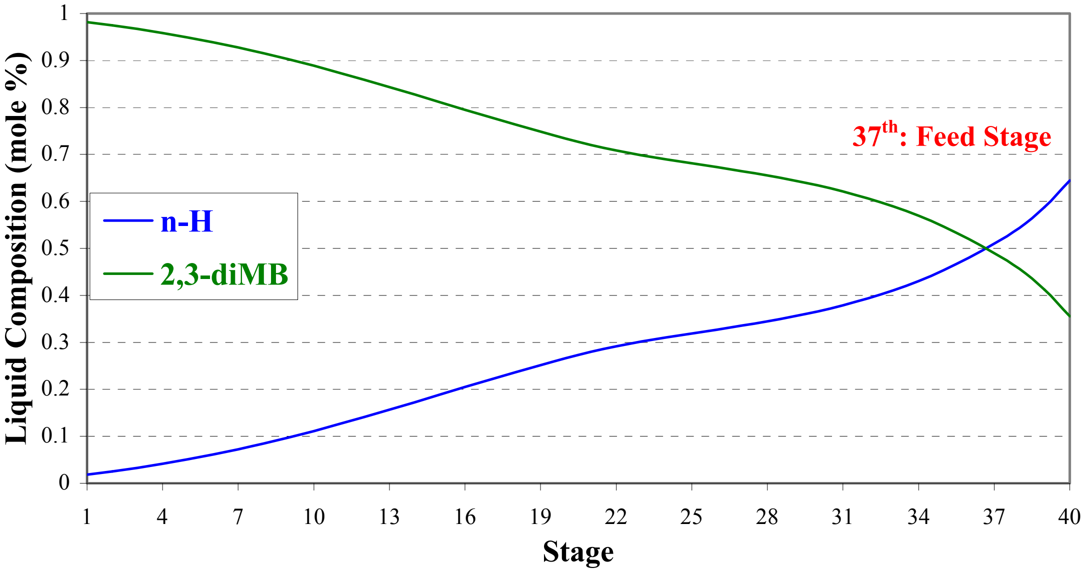


Figure 16. **Reflux Ratio *Vs* Feed Stage for the Reactive Distillation Column. Reaction with Very Fast Catalyst, Approach to Equilibrium. (n-H to 2,3-diMB Isomerization). Desired Product: 2,3-diMB**

(Reflux Ratio: Liquid Down Flow/Distillate Flow Rate;
2,3-diMB = 2,3-di-Methyl-Butane; n-H = n-Hexane;
40-Trays Reactive Distillation Column;
1 reactive tray located at the bottom of the column;
Feed: 10 kmol/hr, 50% each isomer)



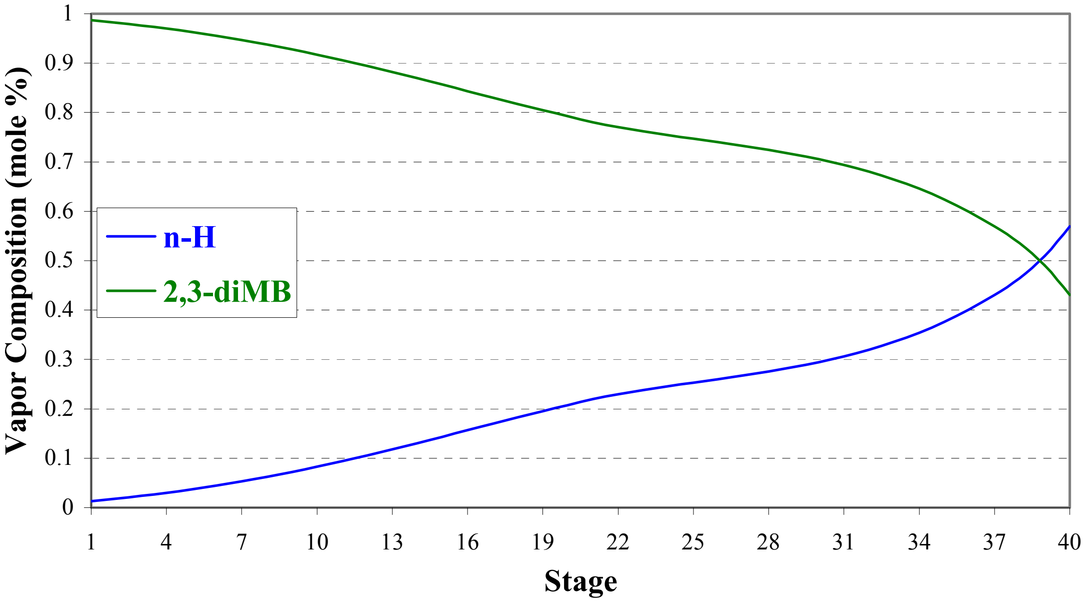


Figure 17. Liquid and Vapor Composition Profiles for the Reactive Column. Reaction with Finite Reaction Rate, 95% Approach to Equilibrium at 58 ºC.

(n-Hexane to 2,3-di-Methyl-Butane Isomerization, Last Line Table 6)

Desired Product: 2,3-diMB

Feed: 10 kmol/hr, 50% each isomer.
(2,3-D-01 = 2,3-di-Methyl-Butane; N-HEX-01 = n-Hexane).
The reactive region goes from the 21st to the 40th tray;
Feed stage: 37th, where liquid composition is closest to feed composition.

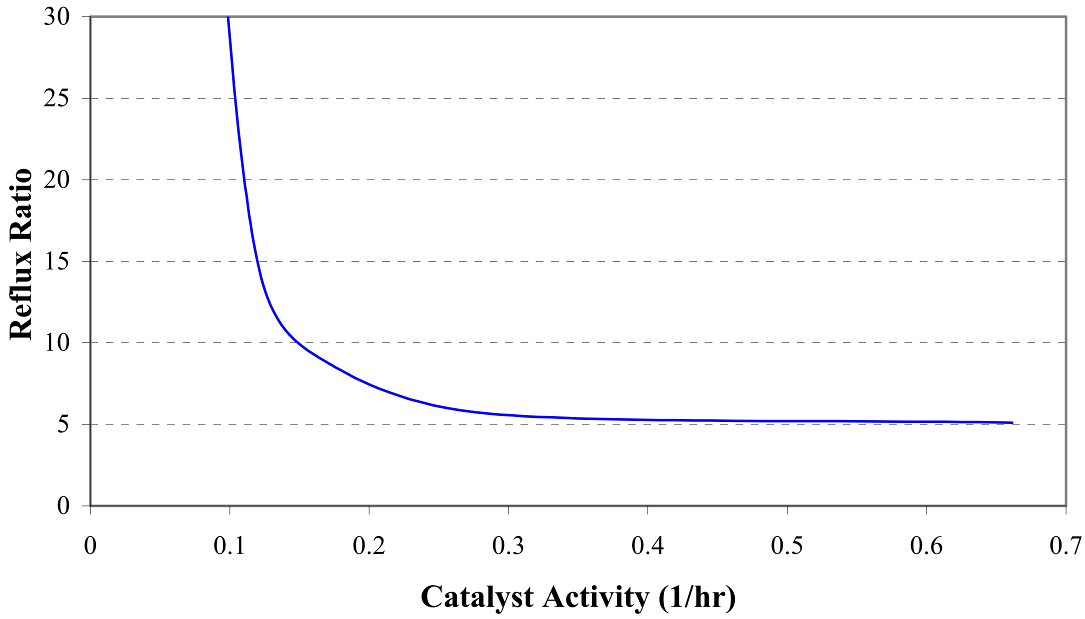


Figure 18. Reflux Ratio *Vs* Catalyst Activity for the Reactive Distillation Column. Reaction with Very Slow Catalyst.

(n-Hexane to 2,3-di-Methyl-Butane Isomerization).

Desired Product: 2,3-diMB

(Reflux Ratio: Liquid Down Flow/Distillate Flow Rate;
2,3-diMB = 2,3-di-Methyl-Butane; n-H = n-Hexane;
40-Trays Reactive Distillation Column, 20 reactive stages from 21st to 40th;
Feed: 10 kmol/hr, 50% each isomer)

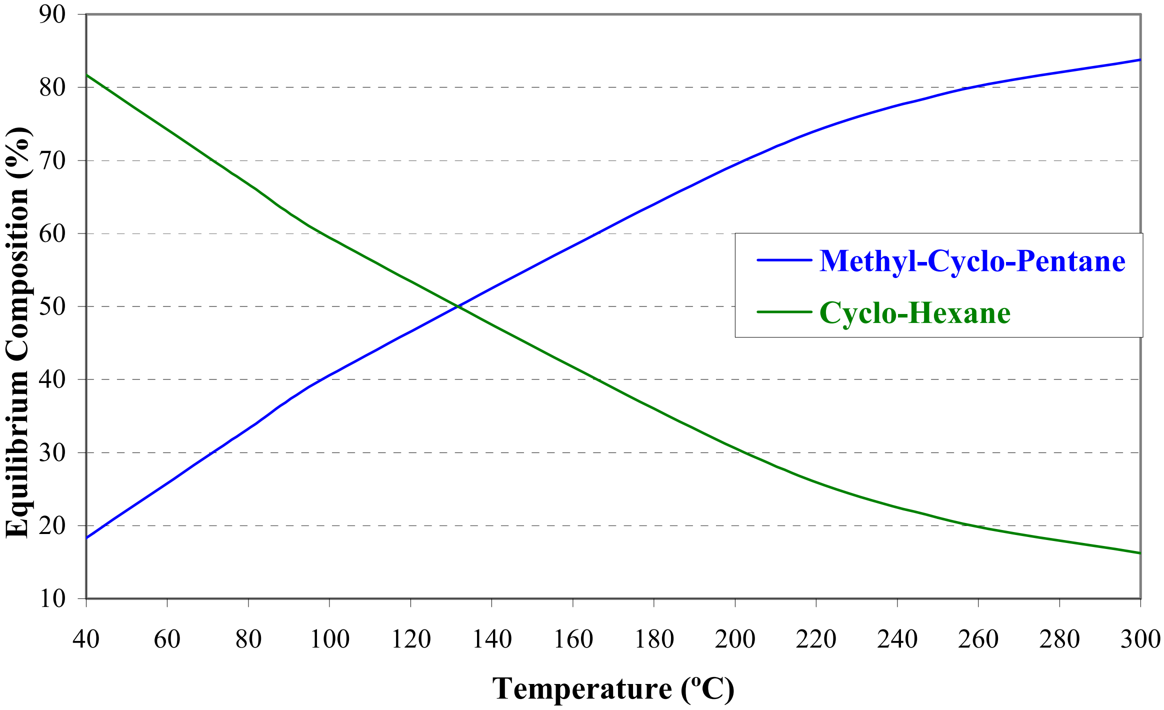
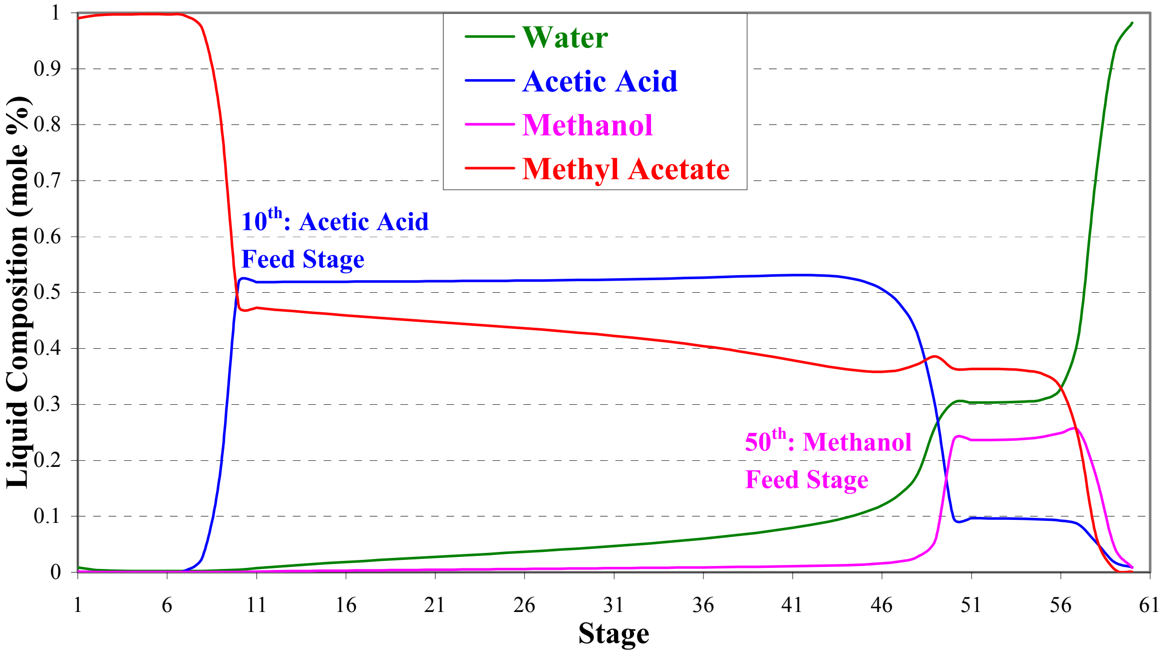


Figure 19. **cyclo-Hexane and Methyl-cyclo-Pentane Reaction Equilibrium Composition *Vs* Temperature.**

(Pressure has no impact)



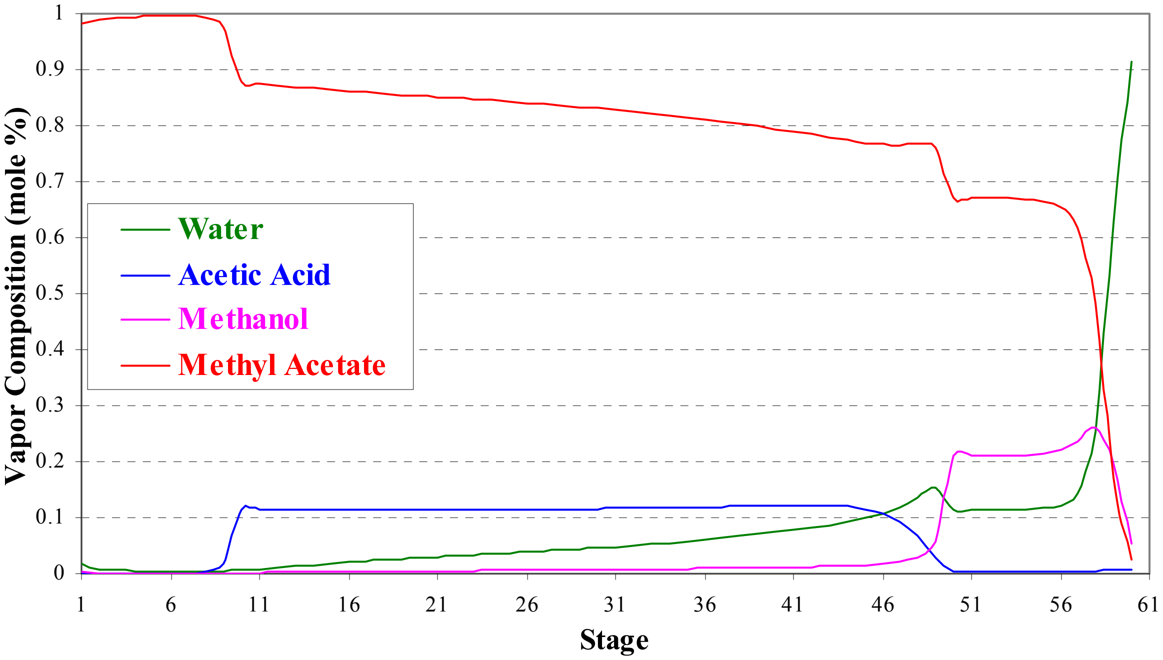


Figure 20. **Liquid and Vapor Composition Change along the Reactive Distillation Column.**

(Methyl Acetate Production).

(RR = 1.7; 60 total trays column, with 49 reactive trays from 12 to 60)

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