Abstract:

Distillation with chemical reaction has received increased attention during the past years as an alternative to conventional processes; reactive distillation has proved to be an economical alternative in many applications (e.g. MTBE and TAME synthesis, production of methyl acetate, manufacture of di-isopropyl ether, oligomerisation of linear butenes and removal of butadiene through dimerisation).

In process synthesis we need to determine the process structure which satisfies our requirements and to determine the optimum operation conditions.

This presentation will describe a new tool for synthesis of reactive distillation columns. The method assesses feasibility of a proposed reactive distillation column, designs the column and allows evaluation of the design for ‘hybrid’ column configurations (columns featuring both reactive and non-reactive sections).

The methodology is based on concepts developed for non-reactive azeotropic distillation and reactive non-hybrid distillation and is applicable for systems with two degrees of freedom.

Reaction equilibrium is assumed on each reactive stage, and vapour-liquid equilibrium is assumed on all stages. The graphical column design method allows fast and relatively simple screening of different reactive distillation column configurations. The methodology is illustrated by application to an ideal reactive system and for MTBE production.
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The first question to be answered is why might we use reactive distillation? What are the benefits, and if there are any, can we always combine reaction and distillation in a single unit?

The answer is double sided. Yes, there are many advantages of using distillation coupled with reaction in a single unit, but certainly we cannot use it for any system: we should consider the particularities of the process, and analyse its constraints.

Here two flowsheets are presented, both using the same raw materials R1 and R2 and producing the same products P1 and P2.

The most obvious difference is in simplicity: in reactive distillation a single column is used to do the same job as 5 units with recycles in a conventional arrangement.
There are certain advantages of using reactive distillation, compared to conventional flowsheets.

The main advantage is the simplification of the flowsheet leading to significant capital savings. Also, due to continuous removal of the products from the reactive zone, an increased conversion is achieved, hence the recycle costs are dramatically reduced. Side reactions can be avoided and consequently selectivity increased due to continuous removal of components from the reactive zone leading to reduced by-product formation.

If the system is non-ideal, its behaviour changes when reaction is present. The reaction can thus be used to deliberately avoid azeotropes (methyl tert-buthyl ether and methyl - acetate production).

Also, in some cases, the heat of reaction can be used in the distillation process to reduce condenser or reboiler duties. This direct heat integration is usually preferred over indirect heat integration, which requires matching temperature and always incurs thermodynamic losses.
Reactive distillation

Constraints and drawbacks

- Volatility constraints
- Residence time requirement
- Scale-up to large flows - liquid distribution problems in packed reactive distillation columns
- Process condition mismatch - the optimum process conditions for distillation (i.e. temperature and pressure) may not match the optimal conditions for reaction

Combining reaction with distillation in one hybrid unit has proved to be in many applications an economical alternative.

However, a reactive distillation column can be used only if the system satisfies certain conditions.

The main constraint in a reactive distillation process is the volatility constraint: the products have to have extreme relative volatilities to make possible their removal from the reaction zone.

The reaction influences the composition on each tray, and thus mass transfer and vapour and liquid loads; for homogeneously catalysed reactions, liquid hold-up is another important design parameter, because the reaction extent is not only a function of tray composition and temperature, but also of residence time.

Considering that the above conditions are met, we have to match the operating conditions; the optimum process conditions for distillation (i.e. temperature and pressure) may not match the optimal conditions for reaction and vice-versa.

Also, there are certain difficulties in scaling-up to large flows: controlling liquid distribution in packed reactive distillation columns is not always an easy task.
If the system and process conditions show that reactive distillation is beneficial, then the structure of the column needs to be chosen.

In reactive distillation synthesis the best column structure is selected which, for given reactants and given specifications of the process, will lead to maximum yield and minimum cost.

The questions to be answered during reactive distillation synthesis are: Should we use a fully reactive column, or a hybrid column (featuring both reactive and non-reactive sections)? Which is the optimum feed distribution pattern? How large should the hold-up be? Would complex configurations increase the performances?

Some of the decisions are simple to make, at least qualitatively, such as using a hybrid column or a fully reactive column, but some require further analysis and screening of many alternatives.

During reactive distillation synthesis we thus have to decide which is the best configuration with respect to our objective and what are the optimum operating parameters in order to implement it.
Current methods for synthesis of reactive distillation processes (1)

- Trial and error
- Optimisation methods (MINLP, Local optimisation, Stochastic optimisation)
- Graphical methods (e.g. McCabe-Thiele, Ponchon Savarit)
- Methods using distillation lines
- Methods using stage composition lines

The methods for synthesis of reactive distillation available at the moment can be mainly divided in five groups: trial and error methods, optimisation methods, graphical methods such as McCabe-Thiele and Ponchon Savarit (developed for binary systems), methods using distillation lines and methods using stage composition lines.
Current methods for synthesis of reactive distillation processes (2)

Trial and error methods

- Commercial simulation packages available
- Suitable once initial process synthesis decisions have been taken - good initialisation necessary
- Iterative and time consuming
- Few guidelines exist for hybrid processes

The first and probably the most common method applied to analyse a reactive distillation process is the trial and error method.

Commercial simulation packages are now available for reactive distillation (Hyprotech, AspenTech), able to deal to a wide range of reactive distillation processes.

However, due to the complexity of the problem, this approach is very time consuming and is based entirely on user expertise as very few guidelines exist about reactive distillation synthesis.

Also, good initialisation is necessary to obtain convergence, making the method suitable only once initial process synthesis decisions have been taken.

Reference:
Current methods for synthesis of reactive distillation processes (3)

Optimisation methods

• MINLP (Mixed Integer Non-Linear Programming) (Ciric & Gu, 1994).
• Local optimisation method ("stage by stage specification method") (Pekkanen, 1995)

Optimal solution, but:
  • Good initialisation required
  • Global optimum not guaranteed
  • Highly non-linear equation system aggravates convergence

• Stochastic network optimisation (Groemping, 2002)
  • Applicable to highly non-linear equation systems
  • Large number of structural varieties can be analysed

Reactive distillation design via optimisation methods is based on the main idea that the system can be represented as a special case of a multiphase reactor network.

Ciric and Gu (1994) formulated a *mixed integer non-linear programming model*, solution of which yields the optimal number of stages, the optimal feed stage location(s) and composition(s), the feed rates and reflux ratios at a minimal annual cost. Pekkanen (1995) described a local optimisation method for the design of reactive distillation (a 'stage by stage specification method'). This approach does not optimise the column as a whole, but the design procedure starts from both column ends and makes the design specifications at each stage as calculation progresses.

The optimisation methods can provide optimal solutions, but a good initialisation is required as highly non-linear equations aggravates convergence; these methods cannot guarantee a global optimum.

Groemping (2002) used stochastic optimisation to optimise a superstructure, which accommodates reaction/distillation units, reboilers, condensers, mixers and splitters, for obtaining the most promising flowsheet structure. Simulated annealing is a powerful optimisation algorithm, but, as all optimisation methods, is very time consuming. It is useful especially in situations when the solution space has several local optima, and in highly combinatorial problems, i.e. for large-scale functions that may assume several discrete configurations.

**References:**
Lee & Westerberg developed Ponchon-Savarit and McCabe Thiele methods (similar to non-reactive distillation), based on difference point concept. Even though applicable only for binary mixtures, these methods constituted a breakthrough in understanding the behaviour of reactive distillation systems.

They extended graphical design methods to ternary and quaternary mixtures, using the visualisation of lever rule.

Graphical methods represent an easy to understand methodology for identifying promising flowsheets and provide a good estimation of starting conditions for a rigorous simulation. They can accommodate double feed columns and hybrid columns. They are, however, restricted by the graphical representation to a limited number of components and their main drawback is that the estimation of reaction extent on each stage is needed.

References:
Current methods for synthesis of reactive distillation processes (5)

Methods using distillation lines

(Barbosa & Doherty, 1988; Bessling et al., 1997)

- Feasible configurations by intersection of distillation lines
- Visualisation of basic underlying phenomena (boundaries)
- Graphical interpretation
  - Limited degrees of freedom
  - Not applicable to multicomponent mixtures (ternary diagrams)
  - Not applicable to columns with both reactive and inert zones

For non-reactive ternary systems, composition profiles are displayed in triangular diagrams to analyse the physical boundaries of a system.

Following this approach, reactive distillation profiles were developed, to visualise the boundaries for separation processes with superimposed reactions. This concept allows an initial assessment of opportunities and limits of reactive distillation.

However, the number of components is limited for this approach, to facilitate the visual interpretation. Also it is not possible to address columns with both reactive and non-reactive zones.

References:
Current methods for synthesis of reactive distillation processes (6)

Methods using stage composition lines

(Groemping, 2002)

• Feasible configurations by intersection of rectifying and stripping stage composition lines
• Discrete nature of staged columns and staged packing accounted for
  ▷ Limited to systems with two degrees of freedom
  ▷ The use of transformed variables restricts its applicability to fully reactive columns (non-hybrid columns)

Using the analogy with the methodology developed for non-reactive columns, intersection of reactive Stage Composition Lines (SCL) were used by Groemping (2002) to assess feasible designs and evaluate the performance of different configurations.

Reactive SCL are continuous lines, as the reflux or reboil ratio can be varied continuously. This is an advantage of SCL over composition profiles, as all points on a SCL are attainable and satisfy the specified product composition.

The methodology is applicable to systems with two degrees of freedom according to the Gibbs phase rule, featuring one or multiple equilibrium reactions, with a single feed and two products. The use of transformed variables restricts the applicability of the method to fully reactive columns.

The method can be applied for feasibility analysis, column design and to quickly evaluate design options.

References:
A number of approaches can be used for the synthesis of reactive distillation processes, each with its own merits and limitations. Some can handle a great depth of modelling, some can address a large number and high complexity of flowsheet structures simultaneously, some are fast and some allow strong user interaction.

In this diagram we ranked the approaches to two important aspects in the synthesis of reactive distillation processes: the variety of flowsheet configurations that they can address simultaneously - displayed on the horizontal axis - and the thermodynamic complexity they can handle - displayed on the vertical axis. The shaded area indicates where the application of a technique is most appropriate. They usually can be applied to a wider range. Stochastic network optimisation, for example, can be applied over the entire range, but there are reasons not to do so, such as required time or limited direct user interaction.

In reactive distillation we face highly complex systems, as both non-ideal VLE models and complex reaction kinetics have to be incorporated. For process synthesis purposes we want to analyse a large variety of structures at the same time. At the other end on the scale, a conceptual approach is desirable, once we have decided to use a specific flowsheet structure. Such an approach would avoid trial and error simulations by screening design options to understand sensitivities and trade-offs and initialise rigorous simulation.
For the synthesis of a single reactive distillation column, optimisation methods proved to be very time consuming, and usually they are more appropriate for analysing a large variety of structures.

Short-cut methods such as Fenske, are not available for reactive distillation columns, and graphical methods developed recently (McCabe-Thiele and Ponchon Savarit) are only applicable to binary mixtures.

The concept of distillation lines and composition profiles visualised in a ternary diagram offered insights about behaviour of reactive distillation systems and allowed application to ternary mixtures. Unfortunately, their applicability to muticomponent mixtures is restricted by the graphical representation.

However, we can calculate and plot composition profiles in a reactive column and make the use of the conceptual design procedures designed for non-reactive, non-ideal mixtures.
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For a non-reactive column, the intersection of composition profiles can be used to assess feasibility of a column.

Starting from fully specified top and bottom product compositions, composition profiles can be plotted stagewise by solving simple algebraic equations (the operating lines equations).

An intersection of rectifying and stripping composition profiles will indicate a feasible design.

But the discrete nature of composition profiles makes it difficult to assess the feasibility if the points on the composition profiles of the rectifying section and the stripping section do not coincide exactly.
An alternative way, which overcomes the disadvantage created by the discrete nature of composition profiles, is using Stage Composition Lines (SCL).

SCL represent the locus of liquid compositions on a given stage number in a column section, for any reflux or reboil ratio.

They contain the same information as composition profiles, only rearranged, and offer the same insights about system behaviour. SCL are the result of solving stagewise similar simple algebraic equations.

The main advantage of using Stage Composition Lines against composition profiles is that because SCL are continuous loci, intersection of stripping and rectifying SCL will always represent a feasible design.
Here are represented the composition profiles for a non-reactive stripping section starting from a fully defined bottom composition. Different reboil ratios are used to generate the profiles. By rearranging the information contained in composition profiles, we can plot a Stage Composition Line, which represents all possible compositions on a specific stage \( m \), for all reboil ratios \( s \).

The Stage Composition Lines are just different representations of composition profiles, but they offer certain advantages in column design procedures, as pointed out by Castillo and Thong.

**References:**
Specifying both top and bottom compositions, stage composition lines for both rectifying and stripping sections can be plotted as showed in the diagram above. An intersection of a stage composition line from the rectifying section with a stage composition line from the stripping section indicates a feasible design.

For example, the two product compositions are feasible and a continuous profile connecting them can be found for a reflux ratio \( r \) of 5.9 and a reboil ratio \( s \) of 2.7 when the column has 20 rectifying stages \( n \) and 15 stripping stages \( m \).
Extension to reactive distillation

Every reaction reduces dimension of composition space according to Gibbs Phase Rule:

\[ \text{DOF} = 1 + C - \Pi - R \]

**DOF** - Degrees of freedom  
**C** - No. of components  
**\( \Pi \)** - No. of phases  
**R** - No. of reactions

For example, for a 4 component system with one reaction, all compositions satisfying chemical equilibrium will be located onto a two dimensional surface.

For non-reactive systems we can use the intersection of composition profiles or stage composition lines to obtain feasible column designs.

But what about reactive systems?

In chemical systems not all compositions are stable. If chemical equilibrium is assumed, then all compositions which satisfy the chemical equilibrium condition are located on the reactive surface. For the system presented, C cannot exist in pure form, as it always decomposes to A and B.

According to the Gibbs Phase Rule, each chemical reaction reduces the dimension of the composition space by one.

For example, for a 4 component system with one reaction, all compositions satisfying chemical equilibrium will be located onto a two dimensional surface.
In reactive distillation, we can calculate and plot composition profiles, as in non-reactive distillation.

All profiles will be confined on reactive surface.

As we can see in the diagrams presented, all composition profiles in a reactive section of a distillation column are located on the equilibrium surface. Using this particularity of reactive systems, we can calculate composition profiles in the same way as for non-reactive distillation.

Here are presented the composition profiles for a reactive rectifying section from two different angles.

References:
Non-hybrid column design for quaternary systems with single reaction

- If reaction takes place in all column sections, all profiles are located on a curved 2D-surface.
- Look only at the reactive surface where all the profiles are located by using the concept of transformed variables.
- Find intersections between rectifying and stripping composition lines in transformed variables, similar to non-reactive ternary systems.


For a non-hybrid column (a fully reactive column), all profiles are located on a curved 2D-surface. But why not look only at the reactive surface, where all the profiles are located? Using the concept of transformed variables, the composition space can be projected onto a lower dimensional space.

Using this concept, Groemping developed a methodology to assess feasibility and to design fully reactive distillation columns by finding the intersection between rectifying and stripping Stage Composition Lines (represented in transformed variables), similar to non-reactive ternary systems.

References:
Mapping composition space using transformed variables (1)

For each reaction, one component - the reference component - can be eliminated from the composition space.

Transformed composition:

\[
X_i = \frac{X_i - \mathbf{v}_i \cdot \mathbf{v}_i^{-1} \cdot X_{\text{ref}}}{1 - \mathbf{v}_i \cdot \mathbf{v}_i^{-1} \cdot X_{\text{ref}}}
\]

(Ung & Doherty, 1995)

Advantage: reaction term is eliminated from the system of equations.

Same form of operating lines as in non-reactive systems

Use back-transformation to obtain details about reaction extent.

Mixtures with two degrees of freedom, even those with more than three components, will have a two-dimensional reaction space; this space can be mapped onto a two-dimensional plane in transformed composition space. For each reaction, one component, the reference component, can be eliminated from the concentration space. Ung and Doherty (1995) introduced the concept of transformed variables, used to map the concentration space in reactive systems. The benefit of using transformed compositions is that the reaction term is eliminated from the system of equations and the modified operating lines will have the same form as for non-reactive columns.

The composition can be mapped back to real space using back transformation. Reaction extent can be then calculated from the mass balance around the stage (or column section).

References:

The equilibrium surface of an etherification reaction \( A + B \leftrightarrow C \) with inert component D is shown in mole fraction space and in transformed composition space. Components A and B are selected as independent components and are used as co-ordinates of the reaction space. Component C is the reference component.

Two edges of the transformed composition space triangle represent the non-reactive binary pairs AD and BD. The third edge represents the equilibrium line of the ternary system A, B, C.
Stage Composition Lines can be plotted in transformed variables in the same way as for non-reactive systems.

Groemping (2002) developed a methodology to assess feasibility and to calculate feasible designs for fully reactive distillation columns using intersections of reactive Stage Composition Lines in transformed space.

The picture illustrates all feasible designs leading to the desired product compositions for the specified range of operating parameters and stage numbers. The designs for minimum reflux ratio, minimum reboil ratio, minimum cost and minimum number of stages are highlighted. Which of the many feasible design options are economically attractive can be evaluated using more or less sophisticated cost models.

References:
The method developed for non-hybrid columns represents a fast and reliable tool for screening different configurations for systems with two degrees of freedom.

Because SCL do not usually intersect in higher dimension space, their application to multicomponent systems is difficult.

For hybrid columns (columns featuring both reactive and non-reactive sections) the direct application of the method is not possible, as non-reactive composition space has a higher dimension than reactive equilibrium space as the non-reactive section operates in the full composition space.

Hybrid columns, columns with reactive core, two feed columns and complex configurations have not been addressed so far. Also, the method is only available for equilibrium reactions.
Current work

! Extend the previous methodology developed for non-hybrid columns to hybrid columns
! Use insights of hybrid distillation processes to restrict the search and assess feasibility of designs

In the current work, we extended the methodology developed for non-hybrid columns in order to accommodate hybrid columns.

The method is then improved by analysing some insights and specific features of hybrid reactive columns, allowing a more rapid screening for feasible designs.
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Conceptual design methods are available for non-hybrid columns

BUT: In some cases, a fully reactive column cannot be used to obtain the desired product.

If the product is not located on reactive surface, it cannot be obtained from a reactive section.

*Example:*

A + B → C with inert D

Pure C cannot be obtained, unless a non-reactive section is used in the column.

Any other pure component - A, B or the inert D - can be obtained from a reactive section.

Many of the design methods available currently consider only fully reactive columns. But in some cases a fully reactive column cannot be used to obtain the desired product.

A pure component can be obtained from a reactive section if it is located on the reactive surface. If the component is not on the reactive surface, then a non-reactive section is necessary to obtain the desired product.

For example, in the system presented, pure C cannot be obtained from a reactive section because it will always decompose into reactants A and B. Pure C can be obtained only if a non-reactive section is used in the column. Components A, B and the inert D are located on the reactive surface, therefore they can be obtained pure from a reactive section.
Hybrid column design for systems with two degrees of freedom

*Use Stage Composition Lines in transformed variables, as defined for non-hybrid columns.*

- Mass balance in transformed variables holds for both reactive and non-reactive sections
  - Non-reactive stages can be considered a special case of reactive stages where reaction extent is zero
- Intersection between a rectifying and a stripping Stage Composition Line indicates a potentially feasible design

For hybrid columns we can apply, with some amendments, the same concepts developed for non-hybrid columns. The main argument for this is that the mass balance in transformed variables holds for both hybrid and non-hybrid columns: non-reactive stages can be considered a special case of reactive stages, with zero reaction extent.

We can plot Stage Composition Lines in transformed variables for both reactive and non-reactive section. However, not all their intersection points will represent a feasible design.

We have to consider that non-reactive space has a higher dimension, and to amend accordingly the feasibility condition.
Hybrid column design for systems with two degrees of freedom (2)

- Reactive SCL are confined to lie on reactive surface
- Non-reactive SCL can lie anywhere in reaction space

Composition space in a non-reactive section has R additional dimensions compared with the composition space of the reactive section.

*R additional feasibility criteria have to be satisfied*
(i.e. mass balance for the reference components at the intersection point)

R - No. of reactions

Because composition space in a non-reactive section has R additional dimensions compared with the composition space of the reactive section (where R represents the no. of reactions), simple intersection of Stage Composition Lines will not indicate feasible designs, but only potentially feasible designs.

For each potential feasible point, R additional feasibility criteria have to be satisfied. Because in transformed variables the reference component is eliminated from the composition space, the additional feasibility criterion is the mass balance for the reference components at the intersection point. This will ensure that all component balances hold for both reactive and non-reactive sections.
For quaternary systems with one reaction:

**Additional feasibility criterion:**

- mass balance for the reference component at the intersection point has to be satisfied.

\[ L_{s,m+1} \cdot x_{s,m+1,\text{ref}} = V_{s,m} \cdot y_{s,m,\text{ref}} + B \cdot x_{B,\text{ref}} \]

**Assumptions:**

- Liquid and vapour flowrates in non-reactive section are constant
- Transformed flowrates in reactive section are constant
- The effect of feed condition on liquid and vapour transformed flowrates is additive
- Constant pressure in the column

For quaternary systems with one reaction, only one additional feasibility criterion has to be satisfied, that is the mass balance for the reference component at all intersection points.

For the design procedure, liquid and vapour flowrates in the non-reactive section are considered to be constant and for the reactive section the transformed flowrates are considered constant. Also, no pressure drop is assumed in the column, and the effect of feed condition on liquid and vapour transformed flowrates is considered to be additive.
Design procedure for hybrid reactive distillation columns

- Choose a set of *fully specified product compositions* \(x_D\) and \(x_B\)
- Set *feed flowrate, reference component composition* and any other parameter between \(D/F, B/F\) or \(x_{F,i} \neq x_{F,ref}\)
- Set the range of *reflux* and *reboil* ratios to be used for generating SCL
- Search for *intersection* of rectifying and stripping SCL in *transformed* variables
- For each intersection found, *apply* the additional *feasibility criterion*
- *Rank feasible designs* which satisfy the additional feasibility criterion using appropriate cost models

The design procedure starts with choosing a set of fully specified product compositions for the top and bottom products.

For the overall mass balance, the following parameters are needed: feed flowrate, reference component composition and one other specification. This specification can be chosen between \(D/F, B/F\) ratios and feed composition for any component other than the reference component. Ranges of reflux and reboil ratios have then to be set in order to generate Stage Composition Lines.

A search for all intersections between rectifying and stripping SCL is then performed; the intersection points indicate potentially feasible designs. For each intersection found, the additional feasibility criterion is applied, and if the condition is satisfied, then the point represents a feasible design. All feasible designs found are then ranked based on total cost.

Total cost is calculated as a sum of annualised capital cost of column (catalyst cost is considered for reactive sections) and utility cost.
In conclusion, the conceptual design methodology allows one to obtain multiple designs, ranked using appropriate cost models, and design details: number of stages, reflux/reboil ratios, column diameter, condenser/reboiler duties and column cost, with very few specifications and practically no intermediate decision steps.

The only parameters required are a set of fully specified product compositions, feed specifications and a set of reflux and reboil ratio values over a defined range.
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The methodology is illustrated using MTBE synthesis.

MTBE is obtained from an etherification reaction between i-butene and methanol. n-Butane is present in the system as an inert. The system behaviour is highly non-ideal, with three binary azeotropes present. One distillation boundary is formed between the three azeotropes, dividing the composition space into two distillation regions. The diagram presents the MTBE system with the three azeotropes and the distillation boundary.

As we have discussed previously, a pure component cannot be obtained from a reactive section if that component is not located on the reactive surface. Therefore, to obtain pure MTBE, which is not located on the reactive equilibrium surface, a non-reactive section is needed in the stripping section.
In transformed variables, with MTBE the reference component, the residue curve map for the MTBE system shows its very complex behaviour. A ternary reactive azeotrope is formed between the three components present, but only one binary azeotrope is formed, between MeOH and n-Butane. The mixture forms, in transformed composition space, four distillation boundaries.
Specifications for design procedure

- Top product composition - close to the quaternary reactive azeotrope
- Bottom product composition - near pure MTBE
- Feed composition for reference component and one other component (i ≠ ref)
  - Feed is assumed to enter the column on last rectifying stage (reactive stage)
- Reflux and reboil ratio ranges for calculating SCL

For the design procedure, a top product composition was chosen close to the quaternary reactive azeotrope and a bottom product composition near pure MTBE. The feed flowrate and feed compositions for the reference component (MTBE) and for n-butane were specified. To generate the Stage Composition Lines reflux and reboil ratios ranges between 0.5 - 20 were chosen.

The feed is assumed to enter the column on the last rectifying stage (reactive stage). Constant molar overflow and constant pressure in the column were assumed.
MTBE Synthesis - Results

Designs are easily evaluated, using appropriate cost models.

From the feasible designs obtained, designs matching specific requirements (i.e. feed quality) can be selected.

Finding the intersections between rectifying and stripping SCL will indicate potentially feasible designs. For each intersection point, the additional feasibility criterion is then applied, and only feasible designs are selected.

As it can be observed from the diagram, not all intersections between SCL for rectifying and Stripping section lead to feasible designs. The small squares indicate the intersection points, which satisfy the additional criterion within a specified tolerance.

Designs are then evaluated and ranked using total cost (different cost for reactive trays is considered).

From the feasible designs obtained, designs matching specific requirements, such as feed quality, can be selected or estimated using simple interpolation between feasible design parameters.

In the diagram above, the solid circles represent two designs matching a saturated liquid feed condition.
Designs details for the best design with minimum cost and for the best design matching saturated liquid feed condition are presented.

The column with minimum cost is a hybrid column featuring 8 reactive rectifying stages and 7 non-reactive stripping stages, with a diameter of 1.2 m. The operating conditions for the column are: feed condition \( q = -0.474 \), reflux ratio 2.3 and reboil ratio 1.35. The column uses 886.8 kW cold utility for the condenser, and 203.6 kW hot utility for the reboiler. The total cost of the column representing the sum of the annualised capital cost and the utilities cost is 175,212 £/yr.

The design matching saturated liquid feed condition is a column with 8 reactive rectifying stages and only 4 non-reactive stripping stages. The column operates with a reflux ratio of 4.8 and reboil ratio of 13.6. Because of the higher reflux and especially reboil ratios, the column duties are much higher: 1556.9 kW for the condenser, and 2052.7 kW for the reboiler. Even though the column features a reduced number of stages (12 vs. 15 in best design case), the total cost is significantly higher: 287,146 £/yr, due to increased reflux/reboil ratios, and hence increased diameter (1.7 m) and duties.

The results obtained are used to initialise rigorous simulation using HYSYS 2.4.
MTBE Synthesis - Rigorous simulation results

Rigorous simulation using HYSYS 2.4 for best design matching $q_F = 1$

**Specifications:**
Feed composition, feed condition $q_F = 1$
8 stages in the rectifying section
4 stages in the stripping section
$r = 4.8, s = 13.6$

<table>
<thead>
<tr>
<th>Component</th>
<th>Simulation results</th>
<th>Conceptual design specifications</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$x_D$</td>
<td>$x_B$</td>
</tr>
<tr>
<td>i-Butene</td>
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<td>0.000969</td>
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<td>n-Butane</td>
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</tr>
</tbody>
</table>

The conceptual design method results show good agreement with simulation.

For the best design matching feed condition $q = 1$ a rigorous simulation using HYSYS 2.4 was performed. A column with 8 stages in the rectifying section and 4 stages in the stripping section was specified. Feed composition, feed condition, reflux and reboil ratios were also specified.

The results, presented in the table above, show good agreement, considering that the system behaviour is highly non-ideal.
1. Motivation and current approaches

2. Conceptual design of hybrid reactive distillation columns using Stage Composition Lines (SCL)
   2.1. Previous work
   2.2. Design methodology using intersections of Stage Composition Lines in transformed variables
      2.2.1. Design procedure
      2.2.2. Application
   2.3. Design methodology using intersections of non-reactive Stage Composition Lines with reactive surface
      2.3.1. Design procedure
      2.3.2. Applications

3. Conclusions

4. Outlook
• Intersections of SCL in transformed variables for non-hybrid columns offer information about potentially feasible designs

• Exhaustive search for intersection for all segments of SCL has to be performed

BUT:

• Each non-reactive SCL has only one point of intersection with reactive surface

• Restrict the search by looking only at the non-reactive SCL intersection points in relation with reactive SCL

Exhaustive search for intersection for all segments of SCL will offer information about potentially feasible designs. For each intersection found, additional feasibility criterion is applied to find feasible designs. But in some cases, if the reflux/reboil intervals are not close enough, the method might fail to satisfy the additional feasibility criterion. This is caused by the linear approximation of Stage Composition Line segments, which is not appropriate sometimes, especially for highly non-ideal systems. To overcome this, very small reflux/reboil ratio intervals should be used, but then the search will be very time consuming.

The methodology states that a continuous composition profile should be possible between the top and bottom product compositions for a column to be feasible. For a hybrid reactive distillation column that means that the intersection point is situated on both non-reactive stripping SCL and reactive rectifying SCL, hence on reactive surface. Because non-reactive SCL are pseudo-linear, each of them will intersect reactive surface in one point, characterised by a specific reboil ratio. For a given composition, each non-reactive SCL has only one point of intersection with reactive surface.

Using this information, we can restrict the search by looking only at the non-reactive SCL intersection points in relation with reactive SCL, which will give us information about feasible designs.
Each SCL intersects reactive surface at a specific reflux/reboil ratio. The set of resulting intersections is a series of discrete points. From this diagram the relative position of non-reactive SCL and reactive surface can be analysed. As we can see in the diagram, not all SCL intersect the reactive surface, meaning that searching for feasible designs for those SCL which do not intersect reactive surface using the previous methodology will lead to unfeasible designs. Instead, we can just calculate the intersection of SCL with the reactive surface, and focus our search only on the intersection points, which will lead to feasible hybrid column designs. And because all points are now located onto reactive surface, no additional criterion is necessary, as the intersection of SCL with reactive surface is calculated in real composition space.
Because all points are located on reactive surface, we can use for simplification and visualisation the concept of transformed variables. We can plot in transformed variables the reactive SCL and the non-reactive SCL, with their intersection points with the reactive surface, as shown in the diagram.

The main drawback of this approach is that the intersection of non-reactive SCL with reactive surface is a set of discrete points, each point representing a stage and its associated reboil/reflux ratio.

That means that intersections of reactive SCL with segments formed by two adjacent points have no physical meaning, as no fractional stages can exist.

However, because the reactive system is usually a highly constrained system, we cannot satisfy all conditions. In this case, feasible designs can be evaluated, by choosing the closest non-reactive point to the intersection
NRint and Rint can be precisely calculated, as the intersection point is located on the reactive stage composition line.

NSint, Sint cannot be precisely calculated, as the line linking points 3 and 4 have no physical meaning, but can be chosen as the closest point to the intersection point 5.

Resulting design
- No. of rectifying stages: NR
- Reflux ratio: Rint
- No. of stripping stages: NS2
- Reboil ratio: S2

In the diagram above, a segment of a reactive SCL containing all possible compositions of the stage NR for reflux ratios between R1 and R2 is represented (solid line). Also, two adjacent points resulting from the intersection of non-reactive SCL with reactive surface are shown. The points are connected with a dashed line. The two points correspond to stage NS1 (with intersection reboil ratio S1) and stage NS2 (with intersection reboil ratio S2).

An intersection between the two lines (point 5) is characterised by NRint, NSint, Rint and Sint. For the intersection point 5, NRint and Rint can be precisely calculated, as the intersection point is located on the reactive stage composition line, which is a continuous line. But NSint, Sint cannot be precisely calculated, as the line linking points 3 and 4 have no physical meaning. However, for design purposes, it can be chosen as the closest point to the intersection.

Hence, a feasible design for the arrangement above will have the following parameters: NR rectifying reactive stages, NS2 stripping non-reactive stages, reflux ratio Rint and reboil ratio S2 (as point 2 is the closest to the intersection point).
The design procedure for the methodology presented is similar to the general methodology using intersection of SCL. A set of fully specified product compositions for the top and bottom products is needed, along with feed specifications: feed flowrate and reference component composition. One other specification is needed to satisfy the degrees of freedom of the system, which can be chosen between D/F, B/F ratios and feed composition for any component other than reference component. Ranges for reflux and reboil ratios have then to be set in order to generate SCL.

For each non-reactive SCL, its intersection with the reactive surface is then calculated.

The next step is find the intersections between reactive SCL and lines linking two adjacent non-reactive points.

For each intersection found, the design details are calculated and all feasible designs found are then ranked based on total cost.
Design method characteristics

! SCL - simple and easy to calculate
! Many systems of interest in reactive distillation are systems with 2 degrees of freedom (type A+B ⇌ C (D) or A +B ⇌ C + D, suitable for method using SCL)
! Feasibility easily evaluated even prior to SCL intersection calculation: if non-reactive SCL do not intersect reactive surface - no feasible designs possible for the specified product compositions
! Method faster in evaluating the feasible designs by restricting the search to potentially feasible points only
! Assumptions of constant molar overflow in the vapour phase and no pressure drop in the column are not fundamental to the approach

There are certain advantages to using SCL and their intersection with reactive surface in conceptual design of hybrid reactive distillation columns.

The main advantage is that SCL are simple and easy to calculate. They are generated by solving stagewise simple algebraic equations (the operating lines) for different reflux/reboil ratios.

Even though the bidimensional intersection of SCL restricts the method application to systems with two degrees of freedom, the methodology has a large applicability, as many systems of interest in reactive distillation are systems with 2 degrees of freedom (such as etherification or esterification reactions), suitable for method using SCL.

The result of the intersection calculation of non-reactive SCL with the reactive surface can provide information about the feasibility of the column even prior to the search for feasible designs: if non-reactive SCL do not intersect with reactive surface, no feasible designs exist for the specified product compositions.

Restricting the search only to feasible points makes the method faster in assessing feasibility and evaluating feasible designs.

Assumptions of constant molar overflow in the vapour phase and no pressure drop in the column are not fundamental to the approach.
1. Motivation and current approaches

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3. Conclusions

4. Outlook
Two case-studies will be presented to illustrate the design methodology.

The first example is an ideal system, where C is produced from reactants A and B, and D is present in the system as an inert. The equilibrium constant for this reaction is 10.

The diagram shows the reactive SCL corresponding to the top product composition and the stripping SCL corresponding to the bottom product composition in transformed variables. Also, the points resulted from the intersection of stripping SCL with reactive equilibrium surface are represented.

As we can see from the diagram, the region of feasible designs is located in a very small area, circled here with a dotted line.
In the diagram above, details of the feasible design region are presented.

For the specified bottom product composition, there are only two points which can lead to feasible designs: point 1 representing the intersection of stage no. 13 with the reactive surface, at reboil ratio $s = 11.55$, and point 2 which results from the intersection of stage no. 14 with the reactive surface, with a corresponding reboil ratio 5.65.

All feasible designs will be located on the dashed line connecting points 1 and 2.
To evaluate the designs generated, simple cost models, based on the heating and cooling demand and the column capital cost (related to the number and the type of stages and internal flow rates), can be used.

For the case analysed, two designs are presented: the best design with minimum cost, and the best design matching saturated liquid feed condition.

The column with minimum cost is a column with 14 reactive rectifying stages and 13 non-reactive stripping stages, with a diameter of 1.6 m. The operating conditions for the column are: feed condition $q = 1.39$, reflux ratio 2.32 and reboil ratio 5.65. The column duties are 780.8 kW for the condenser and 1545.1 kW for the reboiler. The total cost of the column is 427,945 £/yr.

The design matching saturated liquid feed condition, is a column with 10 reactive rectifying stages and 13 non-reactive stripping stages. The column operates with a reflux ratio of 3.55 and a reboil ratio of 5.65. The total cost of the column is 454,368 £/yr.

As we can see, the design configurations are very similar, all feasible points being concentrated for this case in a small region.

The best design configuration matching feed condition $q = 1$ is used to initialise rigorous simulation.
Rigorous simulation results

Rigorous simulation using HYSYS 2.4 for best design matching $q_F = 1$

**Specifications:**
- Feed composition, feed condition $q_F = 1$
- 10 stages in the rectifying section
- 13 stages in the stripping section
- $r = 3.55$, $s = 5.65$

<table>
<thead>
<tr>
<th>Component</th>
<th>Simulation results</th>
<th>Conceptual design specifications</th>
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</thead>
<tbody>
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<td></td>
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</tr>
<tr>
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</tr>
<tr>
<td>D</td>
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</table>

The design method results are in reasonable agreement with simulation.

For the rigorous simulation, a column with 10 stages in the rectifying section and 13 stages in the stripping section was used. A reflux ratio of 3.55 and a reboil ratio of 5.65 were specified.

The table presents a comparison between conceptual design specifications and simulation results. The design method results are in reasonable agreement with simulation.

The differences are caused on one side by the approximation in estimating feasible designs, as there is no exact intersection point for the stripping section, and on other side caused by the assumptions of constant molar overflow and constant pressure in the column.

However, the method represent a fast tool for searching feasible designs, even though the results are not as precise as for non-hybrid columns. A usual run time for an ideal system using maximum 50 stages in each section and maximum 50 reflux/reboil ratio intervals is, using a Pentium IV 1.5 GHz, less than 1 min.
The second example is the highly non-ideal system presented before, the MTBE synthesis.

The rectifying reactive SCL and the points of intersection of non-reactive SCL and the reactive surface are presented. The feasible design region is presented in detail, and we can see that all feasible designs are located between point 1 (10 stripping stages and reboil ratio 2.23) and point 2 (11 stripping stages and reboil ratio 2.24).
For MTBE synthesis, two designs are presented: the best design with minimum cost, and the best design matching saturated vapour feed condition.

The column with minimum cost is a hybrid column featuring 6 reactive rectifying stages and 9 non-reactive stripping stages, with a diameter of 1 m. The operating conditions for the column are: feed condition $q = 0.237$, reflux ratio 1.4 and reboil ratio 2.2. The column condenser duty is 634.5 kW and the reboiler duty is 337.7 kW. The total cost of the column representing the sum between the annualised capital cost and the utilities cost is 166,483 £/yr.

The design matching saturated vapour feed condition, obtained by simple interpolation between feasible designs is a column with 6 reactive rectifying stages and 9 non-reactive stripping stages. The column operates with a reflux ratio of 1.8 and a reboil ratio of 2.2. The total cost of the column is: 173,787 £/yr.

The best design configuration with minimum cost is used to initialise rigorous simulation.

For this non-ideal system, the NRTL model was used for VLE calculation. A usual run time for this system using maximum 50 stages in each section and maximum 50 reflux/reboil ratio intervals is, using a Pentium IV 1.5 GHz, less than 5 min.
Validation using rigorous simulation

Rigorous simulation using HYSYS 2.4 for best design

Specifications:
Feed composition, feed condition \( q_F = 0.237 \)
6 stages in the rectifying section
9 stages in the stripping section
\( r = 1.36, \quad s = 2.23 \)

<table>
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<tr>
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<th>Conceptual design specifications</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( x_D )</td>
<td>( x_B )</td>
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<tr>
<td>i-Butene</td>
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</table>

The results show good agreement; the differences are caused by the limitations of the model, due to assumptions of constant molar overflow and constant pressure in the column.

For the rigorous simulation, a column with 6 stages in the rectifying section and 9 stages in the stripping section was used. A reflux ratio of 1.36 and a reboil ratio of 2.23 were specified.

The table presents a comparison between conceptual design specifications and simulation results. The design method results are in good agreement with simulation; the differences are caused by the limitations of the model, due to assumptions of constant molar overflow and constant pressure in the column.
Conclusions

- The graphical design methodology developed for non-hybrid columns has been extended to hybrid columns
- The methodology can be applied to assess feasibility and to design columns for proposed reactive distillation processes
- The methodology is restricted to systems with two degrees of freedom and single-feed two-product columns
- The method can be applied to both ideal and non-ideal systems

In this work, the graphical design methodology developed for non-hybrid columns has been extended to hybrid columns. The methodology developed can be applied to assess feasibility and design columns for proposed reactive distillation processes using hybrid reactive distillation columns.

Even though the methodology was developed for systems with two degrees of freedom and single-feed two-product columns, it proved to be a fast method to assess feasibility of reactive distillation columns and identify promising designs. The method was illustrated for both ideal and non-ideal systems.
The approach presented offers good opportunities for extending the methodology to columns with a reactive core and two-feed columns, which are often required for reactive distillation. Complex configurations, e.g. side-draw columns, side-stripping or side-rectifying columns, are also worth analysing.

The most drastic assumption of the methodology is the constant molar overflow, reflected in the rigorous simulation results. In future work, the conceptual design methodology will be improved by including the energy balances in the SCL calculation to remove constant molar overflow assumption. Also, a pressure drop profile in the column can be easily implemented.

Kinetically controlled reactions will need to be introduced as well to allow application to a wider range of systems and to allow a more realistic representation of a reactive distillation process.