Reactive distillation
(a) Conventional process

(b) Reactive Distillation
Let us begin by considering a reversible reaction scheme: \( A + B \leftrightarrow C + D \) where the boiling points of the components follow the sequence A, C, D and B.

The traditional flow-sheet for this process consists of a reactor followed by a sequence of distillation columns.

The RD column consists of a reactive section in the middle with nonreactive rectifying and stripping sections at the top and bottom. The task of the rectifying section is to recover reactant B from the product stream C. In the stripping section, the reactant A is stripped from the product stream D.
(a) Conventional process

(b) Reactive Distillation
The most spectacular example of the benefits of RD is in the production of methyl acetate.

The acid catalyzed reaction \( \text{MeOH} + \text{AcO} \leftrightarrow \text{MeOAc} + \text{H}_2\text{O} \) was traditionally carried out using the processing scheme consisting of one reactor and a train of nine distillation columns.

In the RD implementation only one column is required and nearly 100% conversion of the reactant is achieved. The capital and operating costs are significantly reduced.
(a) Reactive distillation concept for synthesis of MTBE from the acid-catalysed reaction between MeOH and iso-butene. The butene feed is a mixture of reactive iso-butene and non-reactive \textit{n-butene}.

(b) Reactive distillation concept for the hydration of ethylene oxide to ethylene-glycol.

(c) Reactive distillation concept for reaction between benzene and propene to form cumene.

(d) Reactive distillation concept for reaction production of propylene oxide from propylene chlorohydrin and lime. The reactive sections are indicated by grid lines.
(a) Conventional co-current contacting in Trickle bed hydrodesulphurisation

(b) Counter-current contacting: Reactive Stripping
Co-current gas-liquid downflow trickle-bed reactors are widely applied for hydroprocessing of heavy oils. This co-current mode of operation is disadvantageous in most hydroprocesses. This is because reactions such as hydrodesulphurisation and hydrogenation are inhibited by hydrogen sulphide formed.

The situation is clearly more favorable in the counter-current mode of operation since in this case the major part of the bed operates in the $\text{H}_2\text{S}$ lean regime.
(a) **Simplification** or elimination of the separation system can lead to significant **capital savings**.

(b) **Improved conversion** of reactant approaching 100%. This increase in conversion gives a benefit in reduced recycle costs.

(c) **Improved selectivity**. Removing one of the products from the reaction mixture or maintaining a low concentration of one of the reagents can lead to reduction of the rates of side reactions and hence improved selectivity for the desired products.
(d) Significantly **reduced catalyst requirement** for the same degree of conversion.

(e) **Avoidance of azeotropes.** RD is particularly advantageous when the reactor product is a mixture of species that can form several azeotropes with each other. RD conditions can allow the azeotropes to be reacted away in a single vessel.

(f) **Reduced by-product formation.**
(g) **Heat integration benefits.** If the reaction is exothermic, the heat of reaction can be used to provide the heat of vaporisation and reduce the reboiler duty.

(h) **Avoidance of hot spots** and runaways using liquid vaporisation as thermal fly wheel.
(a) **Volatility constraints**. The reagents and products must have suitable volatility to maintain high concentrations of reactants and low concentrations of products in the reaction zone.

(b) **Residence time requirement**. If the residence time for the reaction is long, a large column size and large tray hold-ups will be needed and it may be more economic to use a reactor-separator arrangement.

(c) **Scale up to large flows**. It is difficult to design RD processes for very large flow rates because of liquid distribution problems in packed RD columns.

(d) **Process conditions mismatch**. In some processes the optimum conditions of temperature and pressure for distillation may be far from optimal for reaction and vice versa.
Counter-current vapor-liquid contacting in trayed columns
Counter-current vapor-liquid contacting in packed columns
Bubble regime
Foam regime
Froth regime
Spray regime

Decreasing vapor flow rates

Increasing vapor flow rates
Bubble regime: Regime undesirable in commercial applications

Foam regime: Regime at gas flow rates too low for most industrial applications

Froth regime: Usual regime in commercial applications

Spray regime: Regime undesirable in commercial applications
The froth regime is usually to be preferred on the trays because of the desire to maintain high liquid hold-up on the trays. High liquid hold-ups could be realised by use of bubble caps, reverse flow trays with additional sumps to provide ample tray residence time.

In the Eastman process for methyl acetate manufacture specially designed high liquid hold-up trays are used.
Various tea-bag configurations. Catalyst particles need to be enveloped in wire gauze packings and placed inside RD columns.
Horizontally disposed (a) wire gauze gutters and (b) wire gauze tubes containing catalyst.
Fig. 12. Catalyst bales licensed by Chemical Research and Licensing.
Structured catalyst-sandwiches
(a) catalytically active Rasching ring

(b) coated structured packing

(c) fluted tubes
Counter-current vapor-liquid-catalyst contacting in trayed columns. (a) catalyst in envelopes inside downcomers, (b) tray contacting with catalyst placed in wire gauze envelopes near the liquid exit from the downcomers and (c) alternating packed layers of catalyst and trays.
Reactive distillation concept for synthesis of MTBE from the acid-catalysed reaction between MeOH and iso-butene. The butene feed is a mixture of reactive iso-butene and non-reactive n-butene.
Separation of close-boiling mixtures

<table>
<thead>
<tr>
<th>Components</th>
<th>Boiling temperature $T_b$ (K)</th>
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<tbody>
<tr>
<td>1-butene</td>
<td>266.9</td>
</tr>
<tr>
<td>2-butene, <em>cis</em></td>
<td>276.9</td>
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<tr>
<td>2-butene, <em>trans</em></td>
<td>274.0</td>
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<tr>
<td>Isobutene</td>
<td>266.2</td>
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<tr>
<td>n-butane</td>
<td>272.7</td>
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<tr>
<td>Isobutane</td>
<td>261.4</td>
</tr>
<tr>
<td>1,3-butadiene</td>
<td>268.7</td>
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</tbody>
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Fig. 1. Coupled reactive distillation columns for MTBE formation and splitting processes.