# Innovative & Sustainable Chemical-Process Analysis, Design & Synthesis: Targeted process intensification


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**PSE for SPEED**

# Outline

- Process Synthesis
- The importance of PI
- Sustainable Process Synthesis-Intensification
- Objective – stage 3
- Mathematical formulation of Process Synthesis-Intensification
- Concepts and Framework
- Application examples
- Hybrid Distillation Schemes

# The *Process Synthesis* problem

The **objective** of Process Synthesis is to find the best processing route, among numerous alternatives for converting given raw materials to desired products subject to design constraints and predefined performance criteria.

Industry **needs improvements** related to:

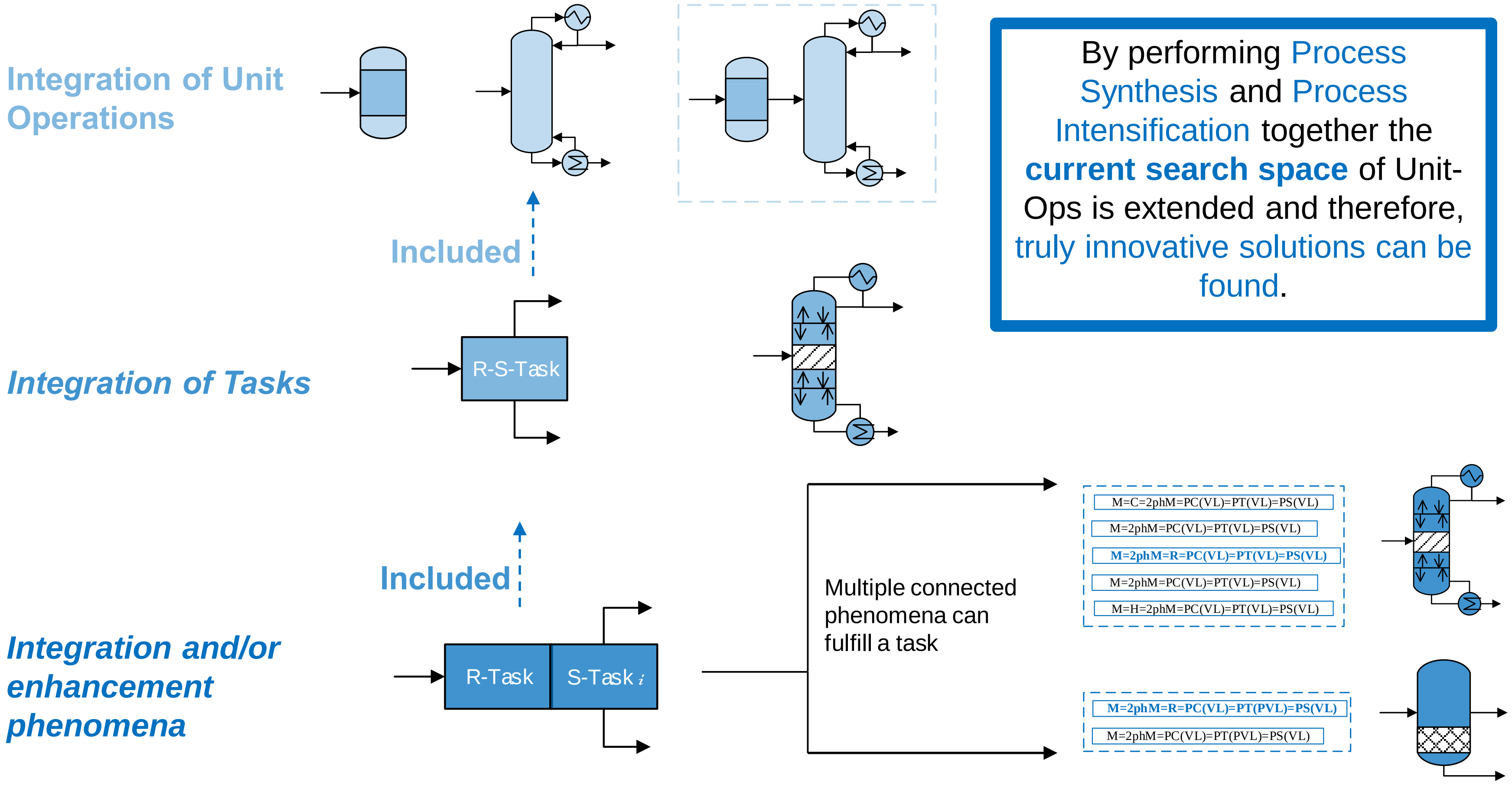
- The use of sustainable technologies/processes
  - ↓ Capital/Operation cost
- The efficient use of raw materials
  - ↓ Waste generation
- The environmental and life cycle issues
  - ↓ Energy consumption

**Question to consider:** How can the search space of process synthesis be expanded to include:

***Well known*+ *Hybrid*+ *Innovative*, *unit operations***

# The merger : Process Synthesis ‘’+’’ Process Intensification

- Process Intensification can be defined as follows:




By performing Process Synthesis and Process Intensification together the **current search space** of Unit-Ops is extended and therefore, truly innovative solutions can be found.

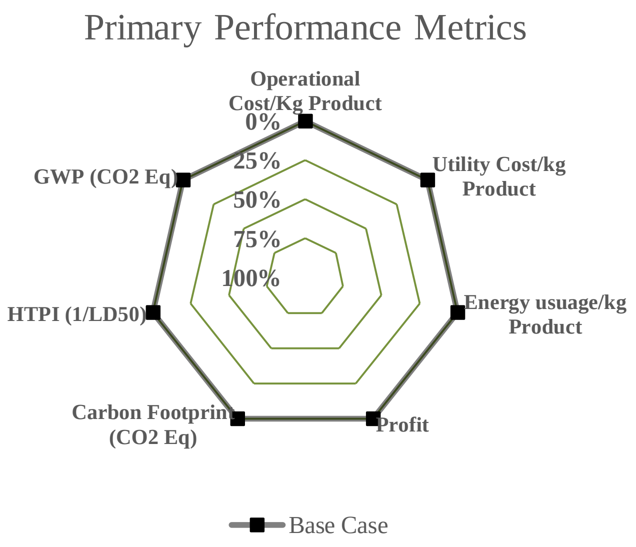
# Sustainable Process Synthesis -Intensification

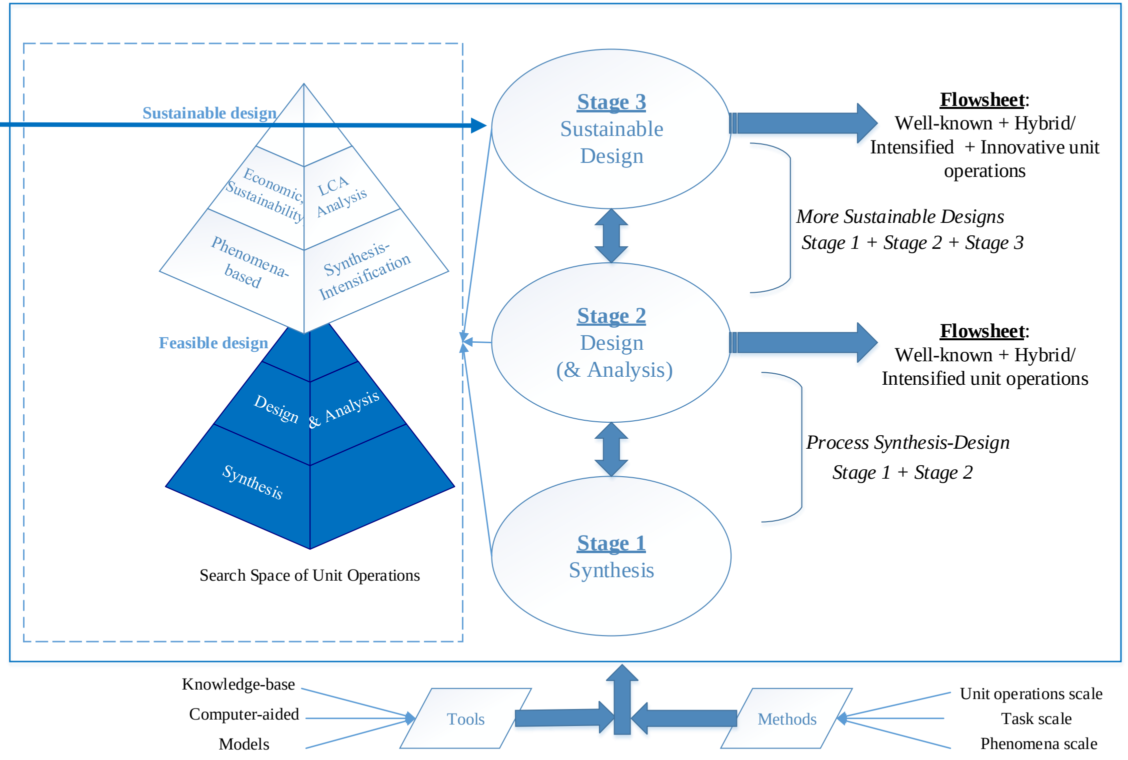
Consists of analyses related to economic and sustainability

Identification of process hot-spots

Identification of design targets

*Satisfied?*




**Synthesis:** *Given*- raw materials and products. *Find*- the processing route

**Design and analysis:** *Given*- the processing route. *Find*- the design

**Sustainable design:** *Given*: the design. *Find*- alternative sustainable processing routes

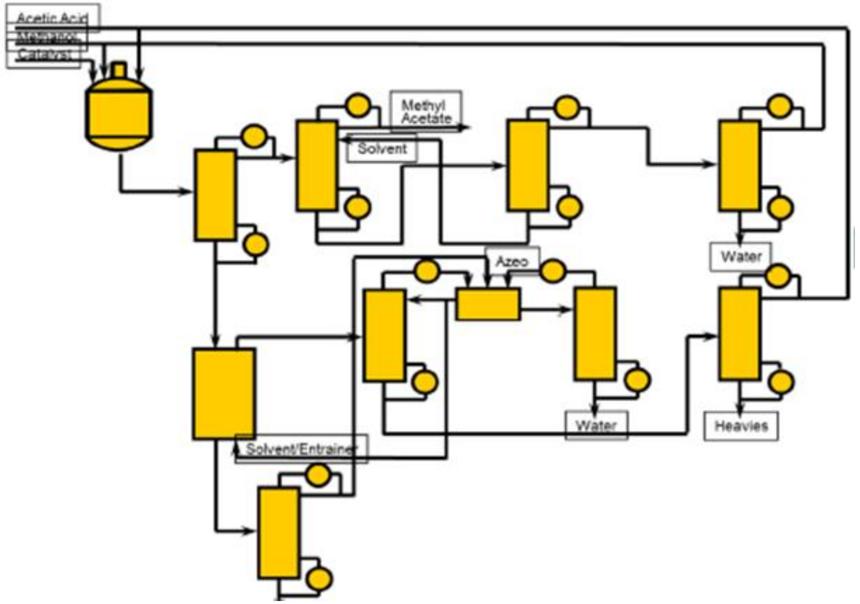
# Objective – stage 3

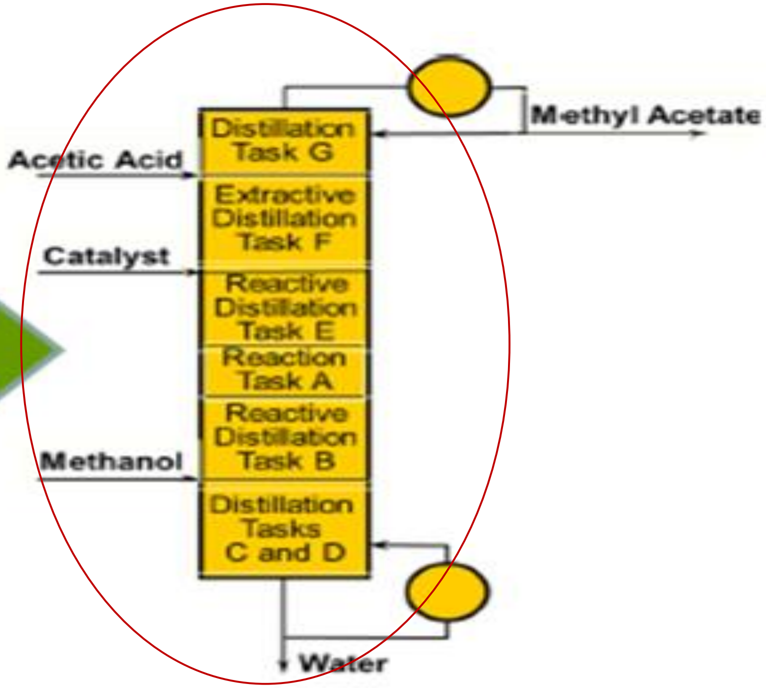
*To present a systematic, computer-aided, multi-level, multi-scale framework, for performing process synthesis-intensification, which operates at the unit operations scale, task scale and phenomena scale for generating more sustainable flowsheet designs, inclusive (where possible) of well-known plus existing/novel intensified/hybrid unit operations.*

**Characteristics of the Framework:**

1. The development of a generic process synthesis-intensification methodology for performing process synthesis and/or intensification
2. Process hot-spot identification through the use of economic, sustainability and LCA analyses
3. Flowsheet generation using a developed integrated task-phenomena based approach systematically generating more sustainable designs from the phenomena scale to the unit operations scale.

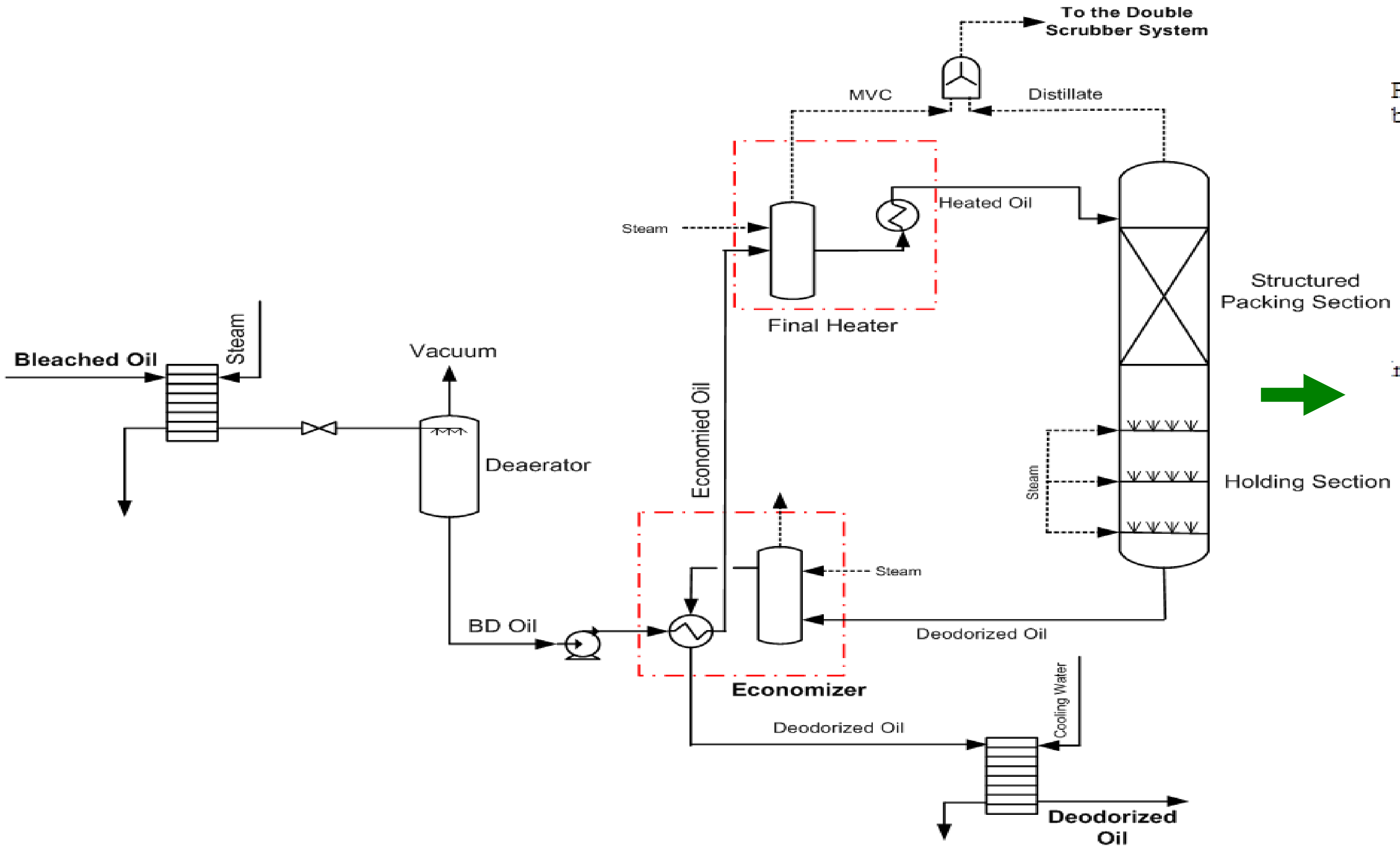
**Target: Intensify (reduce number of operations) as well as operational costs**

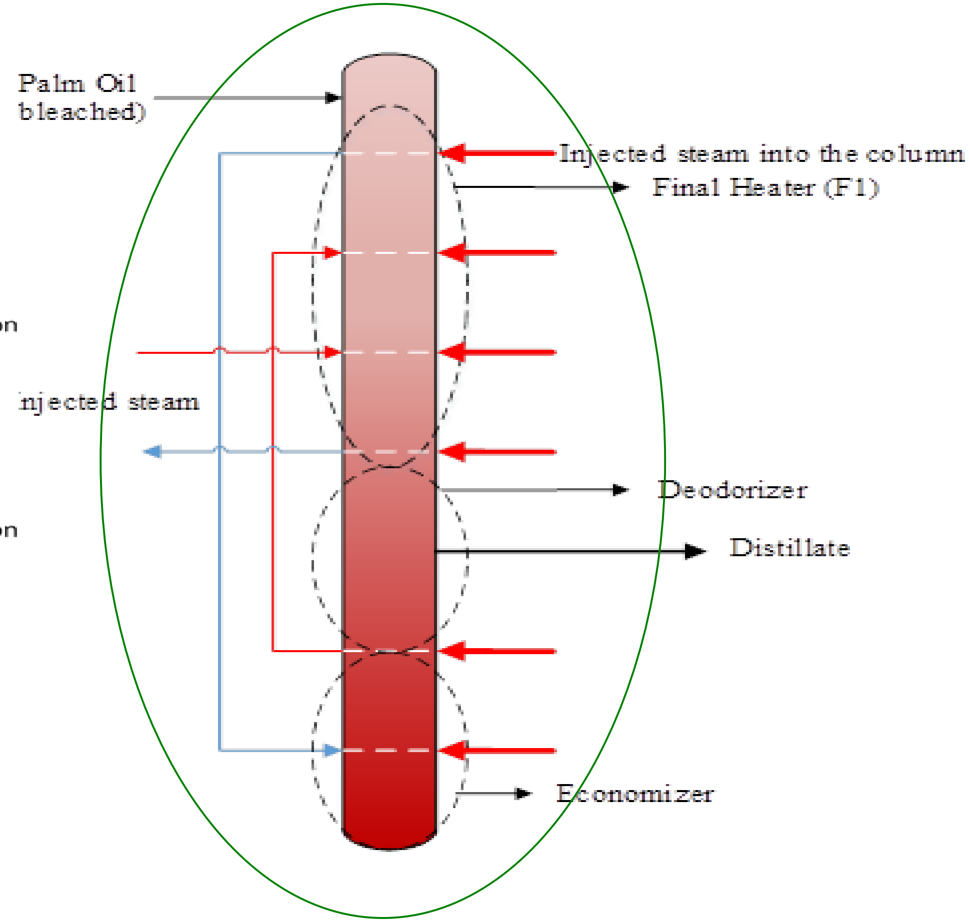



**Methyl acetate in multifunctional reactor (Eastman Chemicals)**

# Industrial example of process intensification




## Deordorization Plant – Alfa Laval, Copenhagen

# Mathematical Formulation: Synthesis-Intensification

***Solution approach: decomposition based***

| | | |
|---|---|---|
| $\min/\max\ f_{obj}^{o} = f_{obj}^{o}(\underline{X},\underline{Y},\underline{d},\underline{z},\underline{\theta})$ | **Objective function (maximized/minimized)** | *** |
| $g(\underline{X},\underline{z},\underline{\theta}) = 0$ <br> $f(\underline{X},\underline{Y},\underline{d},\underline{z},\underline{\theta}) = 0$ | ***Linear & non-linear constraints*** | * |
| $b^{L} \le b_1\underline{X} + b_2\underline{Y} \le b^{U}$ <br> $h^{L} \le h(\underline{X},\underline{Y},\underline{d},\underline{\theta}) \le h^{U}$ | ***Physical constraints & design specifications*** | * |
| $v^{L} \le v(\underline{X},\underline{Y},\underline{d},\underline{\theta}) \le v^{U}$ <br> $w^{L} \le w(\underline{X},\underline{Y},\underline{d},\underline{\theta}) \le w^{U}$ | ***Intensification design specifications & performance criteria*** | * |
| $\underline{Y}^{O} = 0/1, i = 1,2 \ldots n_{y^{O}}, \underline{X}^{O} \ge 0$ | ***Decision variables that are binary-integer*** | ** |

Synthesis-Intensification

*Synthesis-Intensification problem is an MINLP problem because by definition the mathematical formulation consists of linear & non-linear constraints (and/or objective function) and feasible flowsheet alternatives must be selected from among other alternatives*

# Available Synthesis-Intensification Methods

| Method |
| --- |
| Heuristic |
| Mathematical Programming |
| Hybrid |

| Process Synthesis | Feature |
| --- | --- |
| Singh et al., 2010 | Knowledge/data driven-based |
| Quaglia et al., 2014 | Early stage design |
| D'Anterroches, 2006 | Process groups |

| Process Intensification | Feature |
| --- | --- |
| - | - |
| Caballero and Grossmann, 2004 | Dividing wall columns* |
| Peschel et. al, 2012 | Reactor networks* |

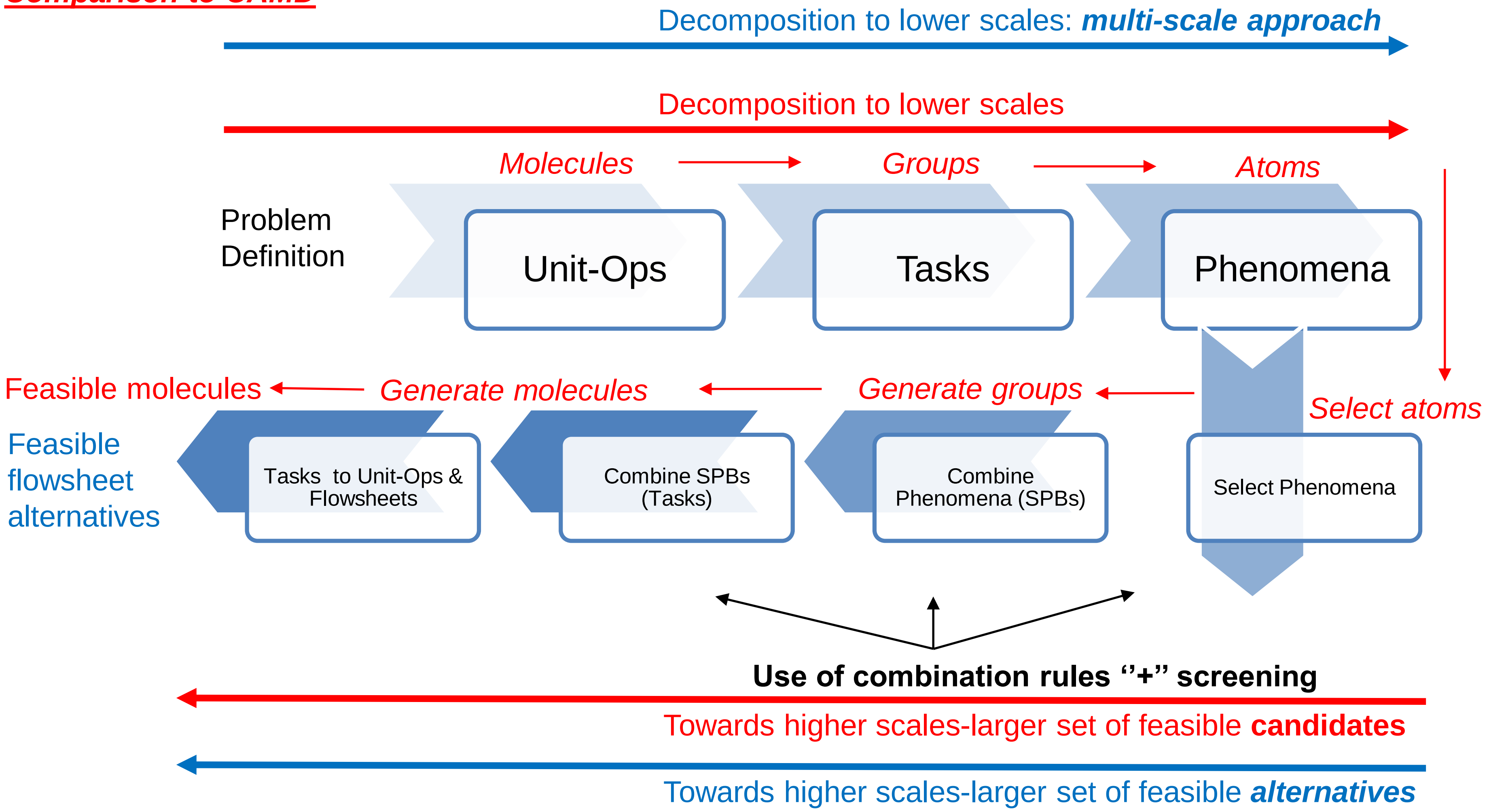
**Applies to intensifying specific parts of a process*

***There is a need for the development of a method for synthesis-intensification of an entire process.***

First version proposed by Lutze 2012.

# Concepts-Phenomena-based Synthesis

***Comparison to CAMD***



# Concepts-Phenomena building blocks

- Most chemical processes can be represented by different combinations of the following 9 phenomena referred to as phenomena building blocks (PBBs) *just as atoms are the building blocks of groups*

**Mixing (M)**

**Two phase mixing (2phM)**

**Phase Contact (PC)**

**Phase Transition (PT)**

**Phase Separation (PS)**

**Heating (H)**

**Cooling (C)**

**Reaction (R)**

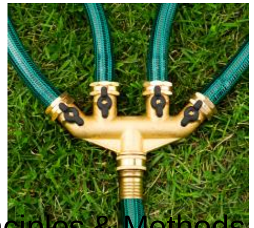
**Dividing (D)**











- PBBs are combined based on combination rules to form ''simultaneous building blocks (SPBs)'' e.g. M=C, M=H, M~~=~~C=H (*thermodynamically infeasible*)

- SPBs are combined to form basic structures that fulfill the objectives of tasks and these structures can then further be expanded to produce operations

## Generation of Flowsheet alternatives using PBBs:

- Recall/Until now: *PBBs→ SPBs→ Basic Structure→ Tasks→ Operations → Unit-ops*
- SPBs are of 2 types: Initiator (I) and Terminator (T)
- Basic structure is a combination of I and T SPBs and fulfill the main objective of a task

*Basic Structure* | *Task fulfilled* | *Unit-Op*

| | |
|---|---|
| **T** | M(VL)=2phM |
| **I** | M(L)=2phM=PC(VL)=PT(PVL)=PS(VL) |
| **T** | M(V)=C |

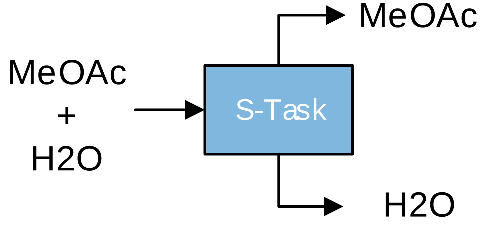
**Basic Structure**

*S-phase-V, Azeo-Yes, Feed Cond.-V*

| | |
|---|---|
| **T** | M(V)=2phM |
| **I** | M(V)=2phM=PT(VV)=PS(VV) |

**Basic Structure**

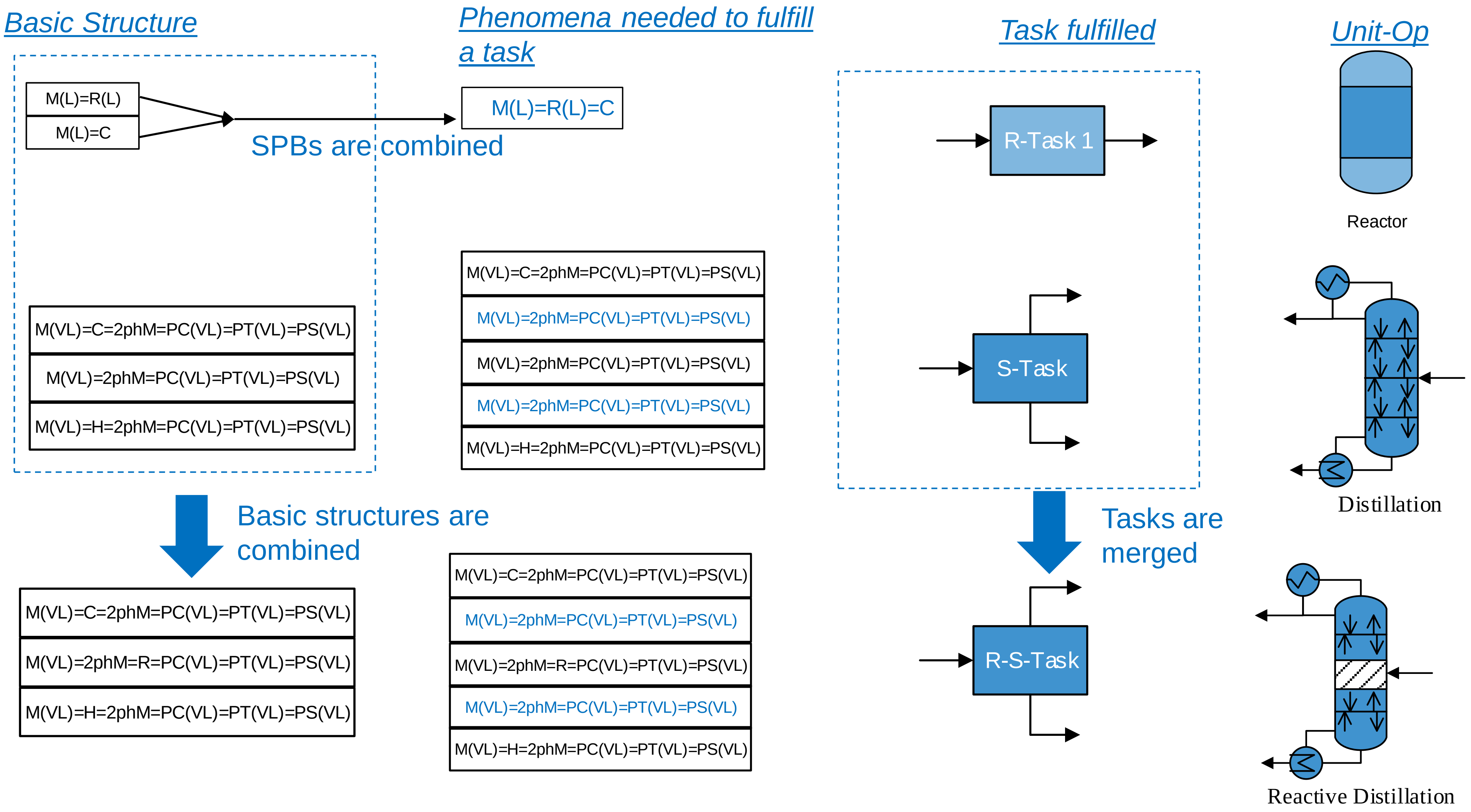
*S-phase-V, Azeo-Yes, Feed Cond.-V*



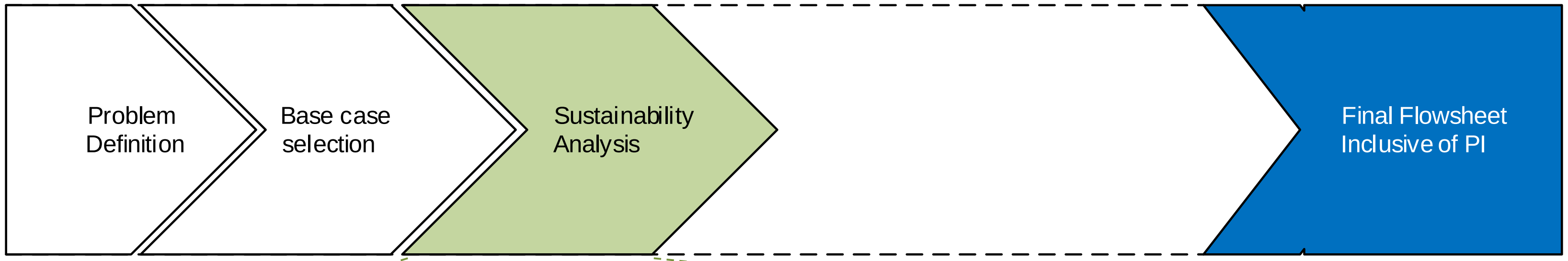

Pervaporation membrane

Vapor permeation membrane

# Concepts

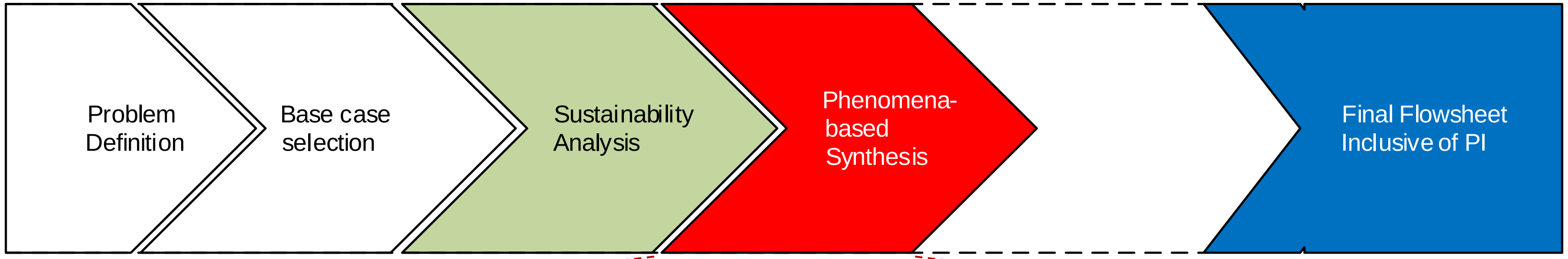

Basic Structure
Phenomena needed to fulfill a task
Task fulfilled
Unit-Op
M(L)=R(L)
M(L)=C
M(L)=R(L)=C
SPBs are combined
R-Task 1
Reactor
M(VL)=C=2phM=PC(VL)=PT(VL)=PS(VL)
M(VL)=2phM=PC(VL)=PT(VL)=PS(VL)
M(VL)=H=2phM=PC(VL)=PT(VL)=PS(VL)
M(VL)=C=2phM=PC(VL)=PT(VL)=PS(VL)
M(VL)=2phM=PC(VL)=PT(VL)=PS(VL)
M(VL)=2phM=PC(VL)=PT(VL)=PS(VL)
M(VL)=2phM=PC(VL)=PT(VL)=PS(VL)
M(VL)=H=2phM=PC(VL)=PT(VL)=PS(VL)
S-Task
Distillation
Basic structures are combined
Tasks are merged
M(VL)=C=2phM=PC(VL)=PT(VL)=PS(VL)
M(VL)=2phM=R=PC(VL)=PT(VL)=PS(VL)
M(VL)=H=2phM=PC(VL)=PT(VL)=PS(VL)
M(VL)=C=2phM=PC(VL)=PT(VL)=PS(VL)
M(VL)=2phM=PC(VL)=PT(VL)=PS(VL)
M(VL)=2phM=R=PC(VL)=PT(VL)=PS(VL)
M(VL)=2phM=PC(VL)=PT(VL)=PS(VL)
M(VL)=H=2phM=PC(VL)=PT(VL)=PS(VL)
R-S-Task
Reactive Distillation

# The Framework



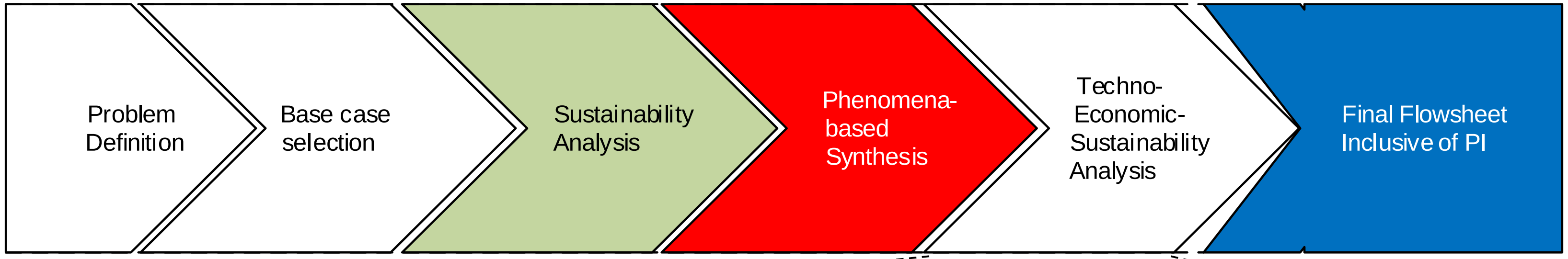

| Input | Output |
|---|---|
| Detailed mass & energy balance data | Performance: Economic, sustainability & LCA analyses |
| Flowsheet Information e.g. no. of streams, unit operations | Process hot-spots & design targets |

# The Framework




| Input | Output |
|---|---|
| Base case design | Flowsheet decomposition→ Phenomena |
| Process hot-spots | Identification of desirable task/phenomena, basic structures |
| Design targets | Phenomena connection→ Flowsheet generation |
| | Flowsheet screening→ Selection |
| | |

# The Framework




| Input | Output |
|---|---|
| Detailed mass & energy balance data *of the screened alternatives* | Equipment sizing & costing |
| | Economic analysis |
| | LCA Analysis |
| | Selection of the best flowsheet alternative based on Fobj |

# The *Multi-level* Framework-Summary

*1st*

**Stage 1-2**

**Scales:** *Unit-Ops+Tasks*

Identify *process hot-spots* & set tagets

*2nd*

Process Analysis

Identification of tasks & PBBs

*Option:* operate at *task* or *phenomena* level

*Option:* phenomena level- generates multiple ways to perform and merge tasks

Generation of flowsheet alternatives

**Scales:** *Tasks+Phenomena*

*PBBs→ SPBs→ Basic Structure→ Operations→ Tasks*

*3rd*

Sustainability Analysis

Intensified flowsheet alternative(s)

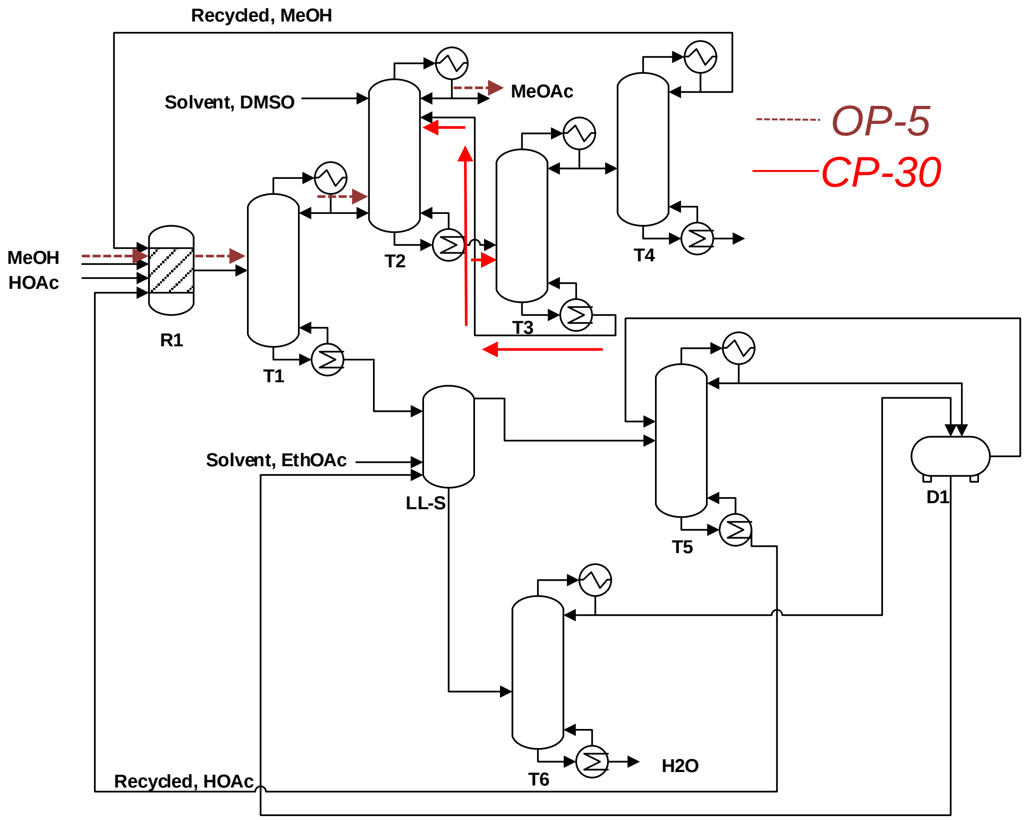
Compare alternatives relative to the base case

# Application:
# Production of Methyl Acetate

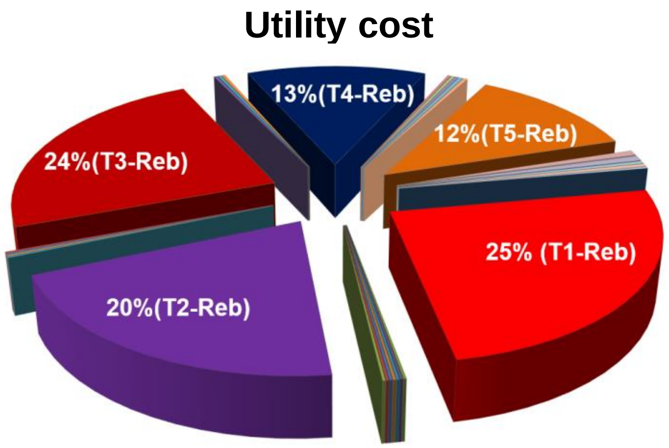
- Problem Definition: The identification of intensified flowsheet alternatives for the production of *Methyl Acetate (MeOAc)* for $HOAc_{conv} \geq 92\%$
  - Reaction (liquid phase): HOAc+MeOH↔MeOAc+H2O
- Fobj: $F_{obj}(C_{Prod}, C_{RM}, C_{Ut}) = Opt\left\{\left(\Sigma m_j C_{Prod,i} - \Sigma m_j C_{RM,j} - \Sigma E_j C_{Ut,j}\right) / m_{Prod}\right\}$
- Base Case Design:
- Sustainability Analysis

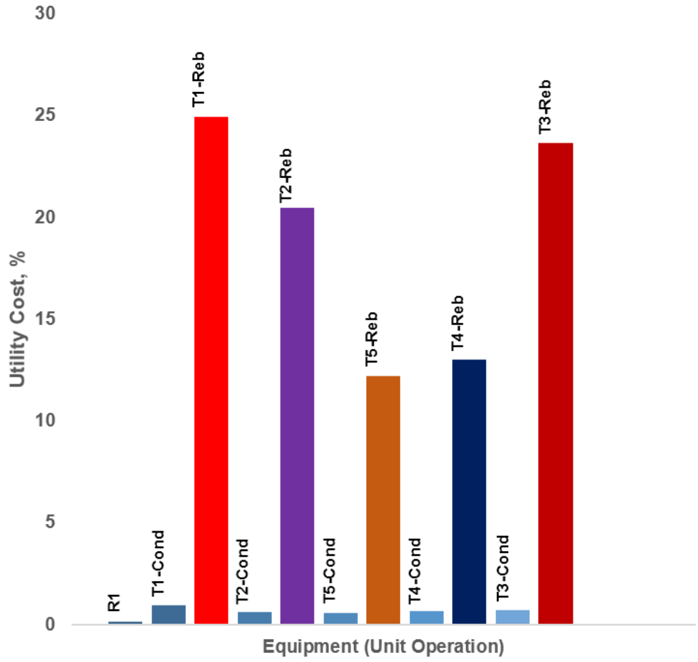
OP-5: Raw Material loss in this path

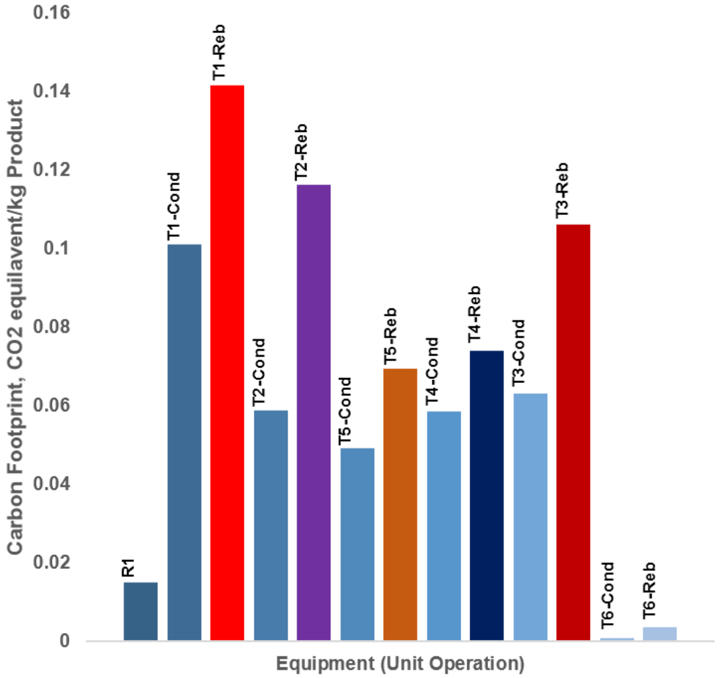
CP-30: High energy consumption in this path



Process ***hot-spots*** from *Economic, Sustainability, LCA* analysis & ***targets***




Economic, Sustainability, LCA:

1. ↑ Utility cost ↑ Energy Demand

2. ↑ Energy Demand ↑ EWC in CP

3. ↑ Energy Demand ↑ CO2 footprint

Targets (e.g.):

1. ↓ Energy demand

2. ↓ Number of Unit-Ops

3. ↑ $HOAc_{conv}$

4. Explore the possibility for using ''hybrid'' Unit-Ops

5. Improve Sustainability & LCA factors

## Process Analysis:

- Thermodynamic insights
- Pure component and mixture properties
- Tasks (already known)→ phenomena

*Excerpt* of properties used for the generation of the binary ratio matrix

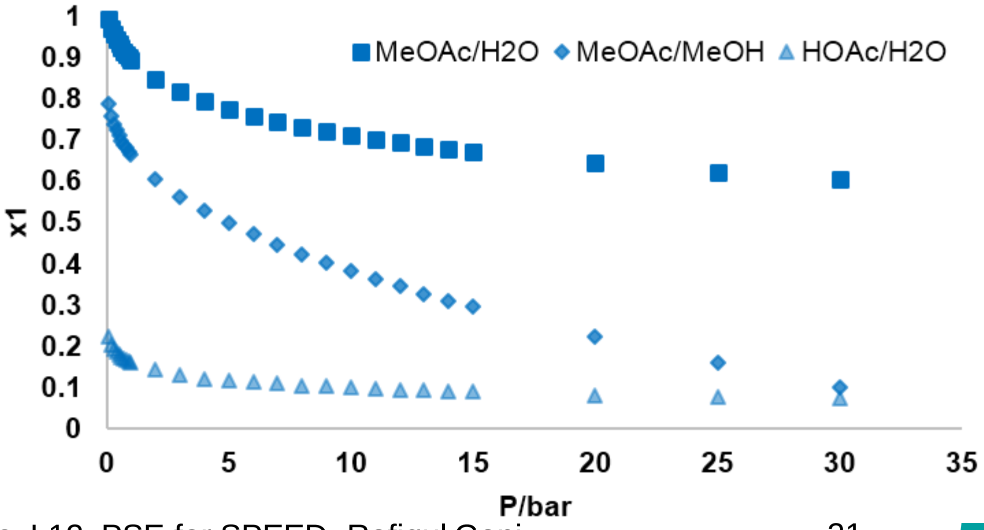
| $r_{ij}$ | MW | Tm | Tb | VP | RG | VdW | VM | SolPar |
|---|---|---|---|---|---|---|---|---|
| MeOH/HOAc | 1.87 | 1.65 | 1.16 | 8.1 | 1.68 | 1.53 | 1.42 | 1.56 |
| MeOH/MeOAc | 2.31 | 1 | 1.02 | 1.7 | 1.93 | 1.96 | 1.97 | 1.53 |
| MeOH/H2O | 1.78 | 1.56 | 1.1 | 5.31 | 2.52 | 1.76 | 2.25 | 1.62 |
| HOAc/MeOAc | 1.23 | 1.65 | 1.18 | 13.8 | 1.15 | 1.28 | 1.39 | 1.02 |
| HOAc/H2O | 3.33 | 1.06 | 1.05 | 1.52 | 4.24 | 2.69 | 3.19 | 2.52 |
| MeOAc/H2O | 4.11 | 1.56 | 1.13 | 9.02 | 4.87 | 3.44 | 4.42 | 2.47 |

***MW-*** *molecular weight*
***Tm-*** *normal melting point*
***Tb-*** *normal boiling point*
***VP-*** *vapour pressure*
***RG-*** *radius of gyration*
***VDW-*** *Van der Waals volume*
***VM-*** *molar volume*
***SolPar-*** *Solubility parameter*

Hints separation based on molecular size possible

| Task | Component | PBBs |
|---|---|---|
| R-Task | HOAc+MeOH | M,R,C |
| S-Task-1 | $HOAc_{LK}$+$MeOH_{HK}$ | M,2phM,H,C,PC,PT,PS by VL |
| S-Task-2 | $MeOAc_{LK}$+$MeOH_{HK}$ (+*Solvent*) | M,2phM,H,C,PC,PT,PS by VL |
| S-Task-4 | $MeOH_{LK}$+$Solvent_{HK}$ | M,2phM,H,C,PC,PT,PS by VL |
| … | … | … |

LK-Light key
HK-Heavy key

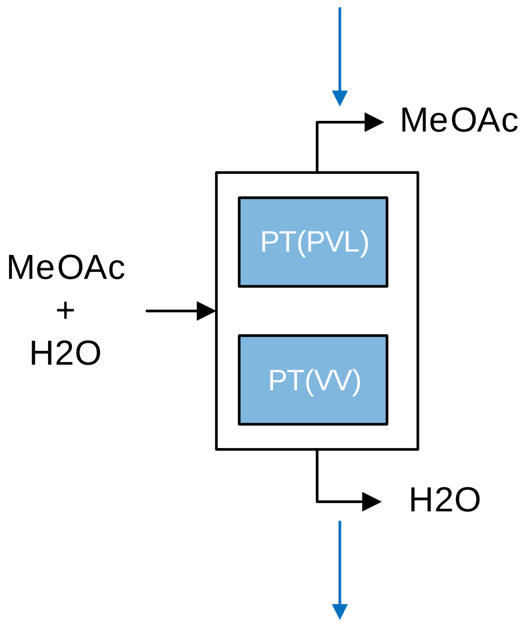


## Identification of tasks and PBBs:

- Example, Separation of MeOAc/H2O azeotrope
- Identify PBBs which fulfill the task in multiple ways
- Identified PBBs search space:
  - R, $M_l$, $M_{FL}$, $M_R$ $M_V$, 2phM, PC(VL), PT(VL), PT(PVL), PT(VV), PS (VL), PS(VV), D, H, C-15 in total
  - All possible combinations- 16278
  - Reduced to 64-combination rules
    - PC(VL)↔PT(VL): *M=2phM=PC(VL)=PT(VL)*: S-Task
    - R↔PT(VL): *M=R=2phM=PC(VL)=PT(VL)=PS(VL)*: **R-S Task**

      *that is merged R-Task and S-Task*

*Thermodynamic insights*




*Represents separation through a membrane*

## SPBs

M(L)=R(L)

M(L)=C

M(L)=2phM=PC(VL)=PT(PVL)=PS(VL)

M(VL)=2phM=R=PC(VL)=PT(VL)=PS(VL)

M(V)=2phM=PT(VV)=PS(VV)

## Basic Structures

M(L)=R(L)=C

M(VL)=2phM

M(L)=2phM=PC(VL)=PT(PVL)=PS(VL)

M(V)=C

M(VL)=2phM

M(V)=2phM=PC(VL)=PT(VV)=PS(VV)

M(L)=H

M(VL)=C=2phM=PC(VL)=PT(VL)=PS(VL)

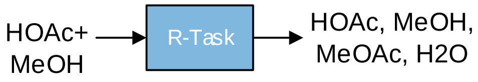
M(VL)=2phM=PC(VL)=PT(VL)=PS(VL)

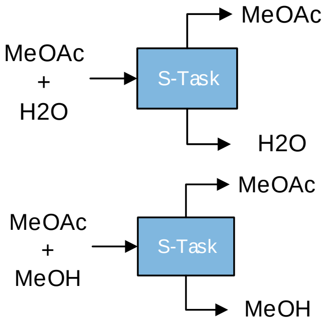
M(VL)=H=2phM=PC(VL)=PT(VL)=PS(VL)

**Note:** The objective is to convert input (HOAc + MeOH) to output( MeOAc + H2O). One basic structure (unless merged) will not achieve this

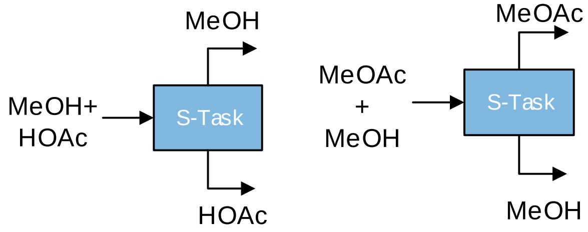
**Note:** This basic structure fulfills two S-tasks

## Task fulfilled

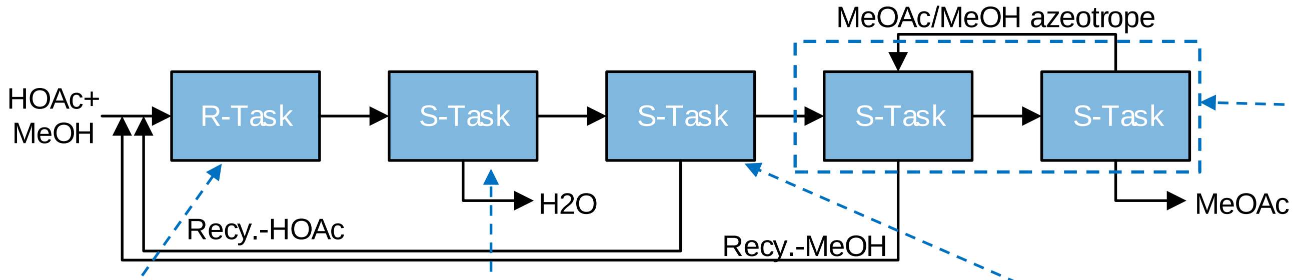



**Note:** Two tasks can be performed in multiple ways using 2 basic structures




## Flowsheet alternative (task-based)



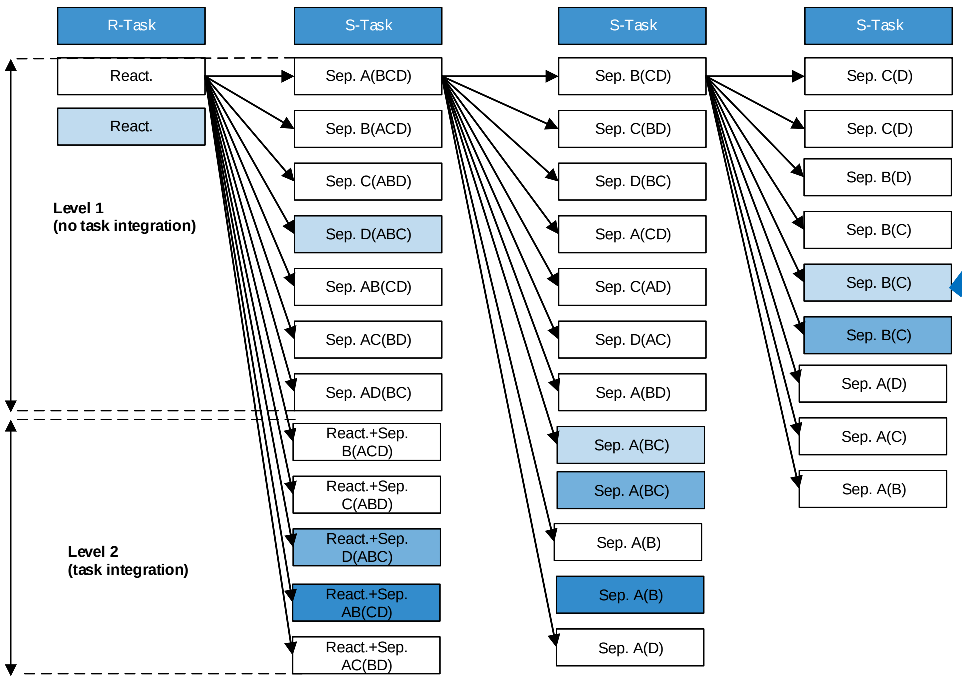

Separation between MeOAc/MeOH is feasible

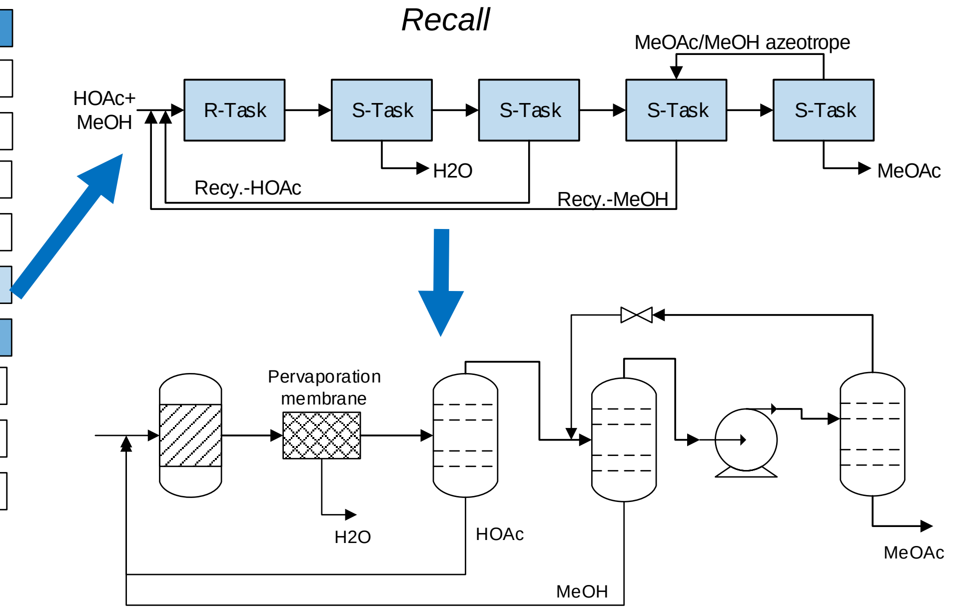
Change of state of raw materials, a reaction task is identified

Azeotrope MeOAc/H2O,H2O in 2 of 3 azeotropes removal of H2O is beneficial

Separation between MeOH/HOAc is feasible

Basic structures fulfill the objective of a task. Therefore from a task-based superstructure one can select the feasible tasks.




Flowsheet alternative 2

**Recall:**

M(L)=R(L)

M(L)=C

M(VL)=2phM

M(L)=2phM=PC(VL)=PT(PVL)=PS(VL)

M(V)=C

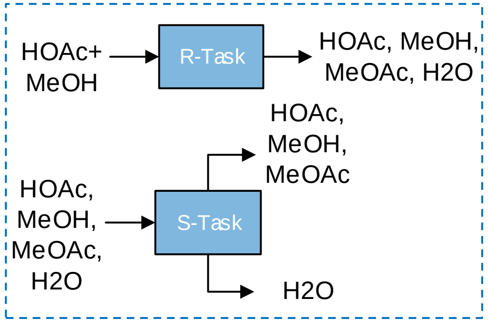
M(VL)=2phM

M(VL)=R(L)=2phM=PC(VL)=PT(PVL)=PS(VL)

M(L)=C

Properties:

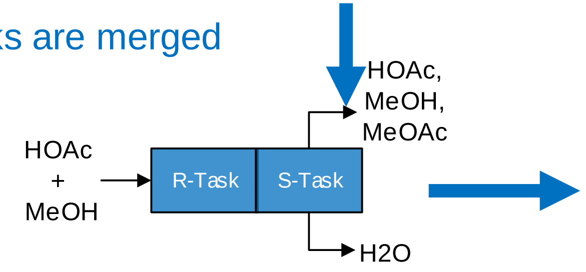
- Esterification reaction
- Azeotropes present
- H2O by-product

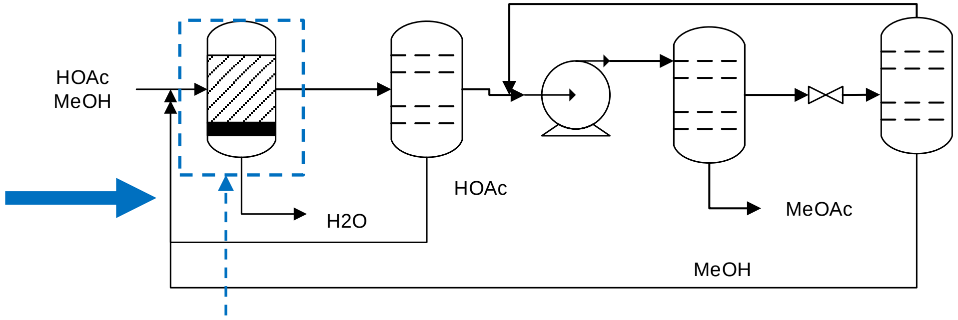



Tasks are merged

Consider: Combination of basic structures?

Basic structures are combined

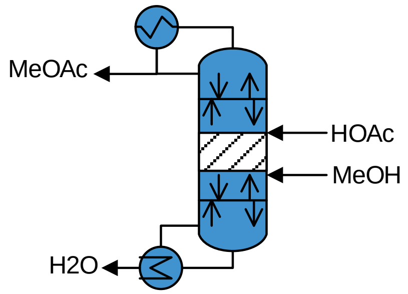




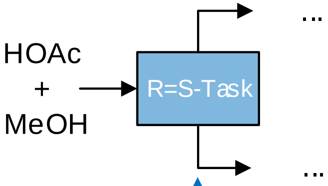

Membrane reactor

Flowsheet alternative 4

***Note:*** A RD superstructure has been investigated to find the feasible RD alternative




Flowsheet alternative 9 (RD)




***Recall:***

M(L)=R(L)

M(L)=C

M(VL)=2phM

M(L)=2phM=PC(VL)=PT(PVL)=PS(VL)

M(V)=C

M(VL)=C=2phM=PC(VL)=PT(VL)=PS(VL)

M(VL)=2phM=PC(VL)=PT(VL)=PS(VL)

M(VL)=H=2phM=PC(VL)=PT(VL)=PS(VL)

Consider: Can reaction and separation be further combined?

Basic structures are combined

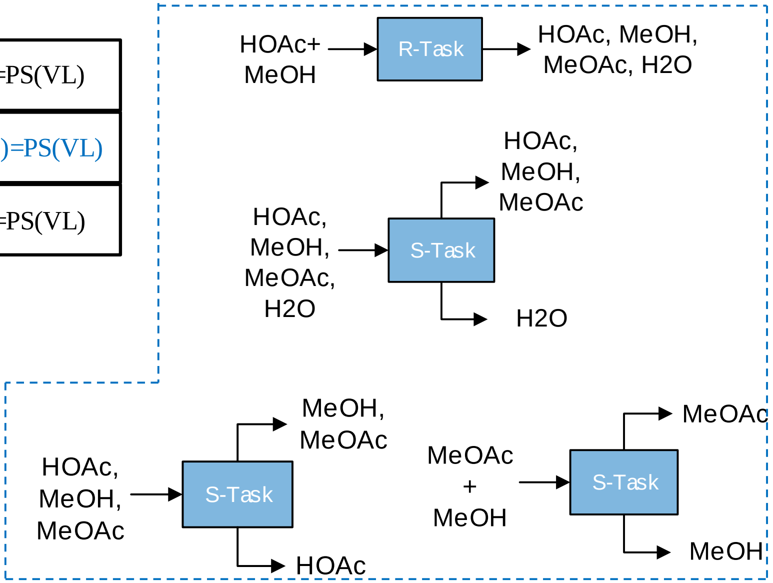
M(VL)=C=2phM=PC(VL)=PT(VL)=PS(VL)

M(VL)=R=2phM=PC(VL)=PT(VL)=PS(VL)

M(VL)=H=2phM=PC(VL)=PT(VL)=PS(VL)

Properties:
- Equilibrium reaction
- Esterification reaction
- Liquid phase reaction
- Azeotropes present

Tasks are merged



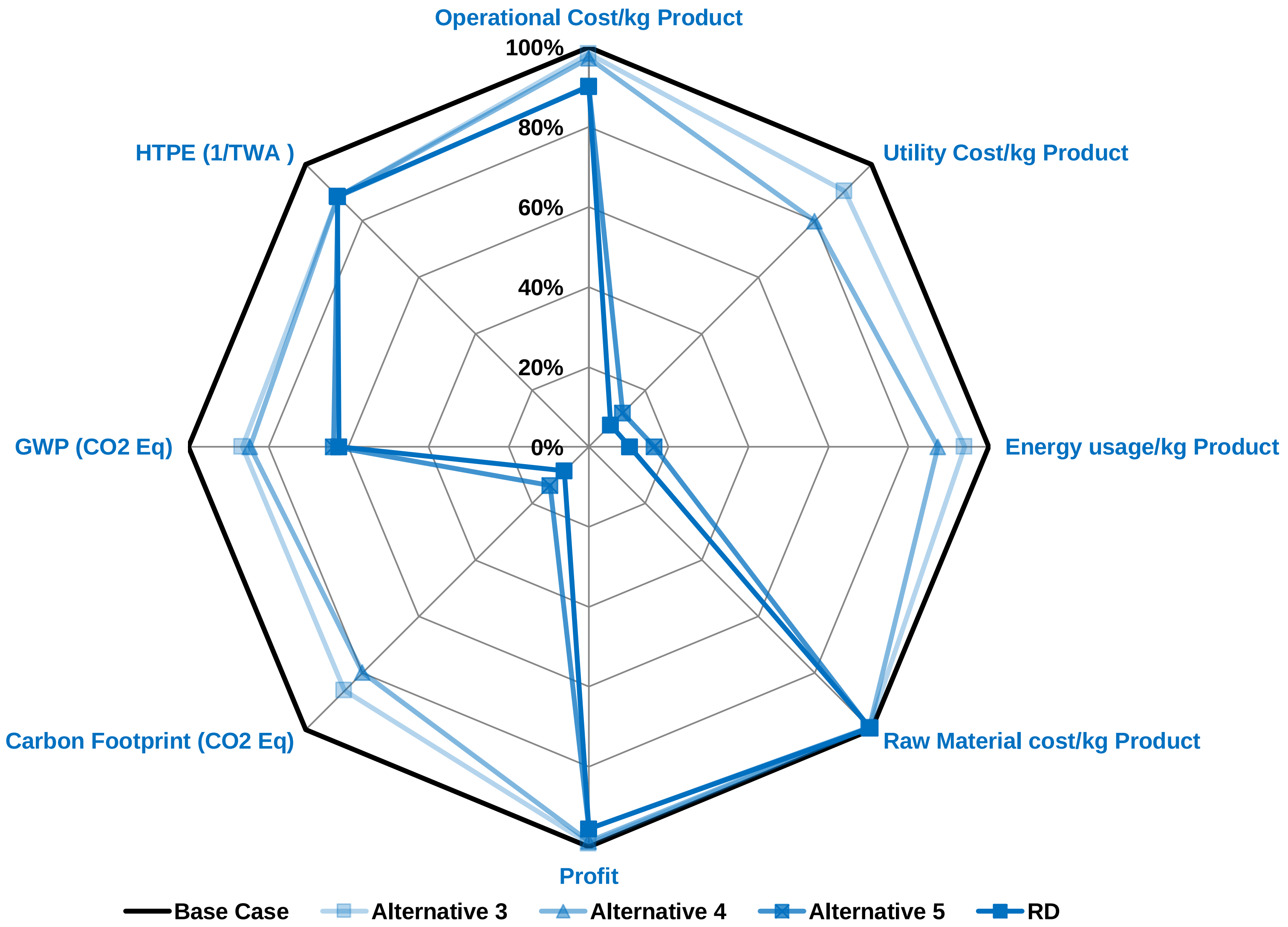
# Sustainability Analysis: comparison of alternatives

| **Primary Performance Metric** | **Design** | | | | |
|---|---|---|---|---|---|
| | Base Case | Alternative 3 | Alternative 4 | Alternative 5 | RD |
| *Energy Usage/kg MeOAc* | 21.88 | 20.57 | 19.12 | 3.60 | 2.225 |
| *Utility Cost/kg MeOAc* | 0.10 | 0.09 | 0.08 | 0.01 | 0.01 |
| *RM Cost/kg MeOAc* | 0.88 | 0.87 | 0.87 | 0.87 | 0.87 |
| *Profit/kg MeOAc (Fobj)* | 2.06 | 2.08 | 2.09 | **2.16** | **2.16** |

- Recall Targets
  - Reduce energy demand-Yes
  - Reduce number of Unit-Ops-Yes
    - Base Case = **9**, Alternative 3 = **5** Alternative 4 = 4, RD = **1**
  - Explore the possibility for using ‘’hybrid’’ Unit-Ops-Yes
  - Improve Sustainability & LCA factors-Yes

- ***TARGETS HAVE BEEN MET***

# Global Picture



Starting point for synthesis-intensification: reaction information

Consider the reaction synthesis path: DME+CO↔MeOAc

Reaction type: carbonylation
100% atom efficiency

***SPBs***

| |
|---|
| Mv=R(V) |
| Mv=H |

| |
|---|
| M(VL)=2phM=R=PC(VL)=PT(VL)=PS(VL) |

***Basic Structures***

| |
|---|
| Mv=R(V)=H |

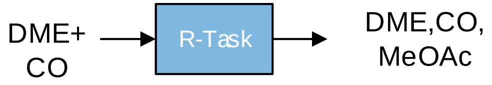
| |
|---|
| M(VL)=2phM=R=PC(VL)=PT(VL)=PS(VL) |

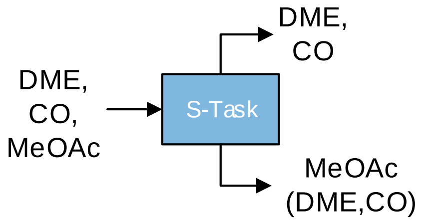
| |
|---|
| M(VL)=C=2phM=PC(VL)=PT(VL)=PS(VL) |
| M(VL)=2phM=PC(VL)=PT(VL)=PS(VL) |
| M(VL)=H=2phM=PC(VL)=PT(VL)=PS(VL) |

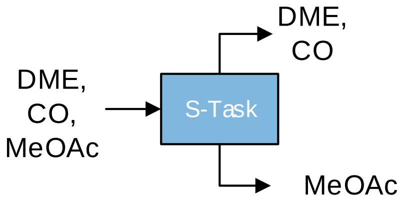
Basic structures are combined

***Note:*** The objective is to convert input (DME + CO) to output( MeOAc. One basic structure (unless merged) will not achieve this

***Task fulfilled***

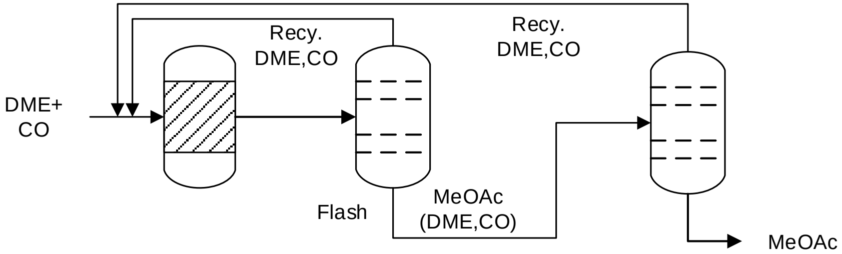


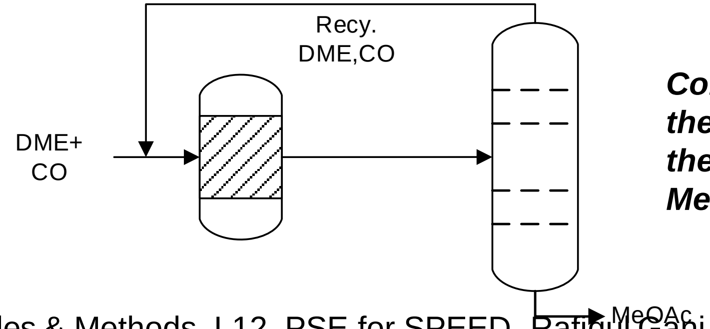




Tasks are merged

***Flowsheet alternative***



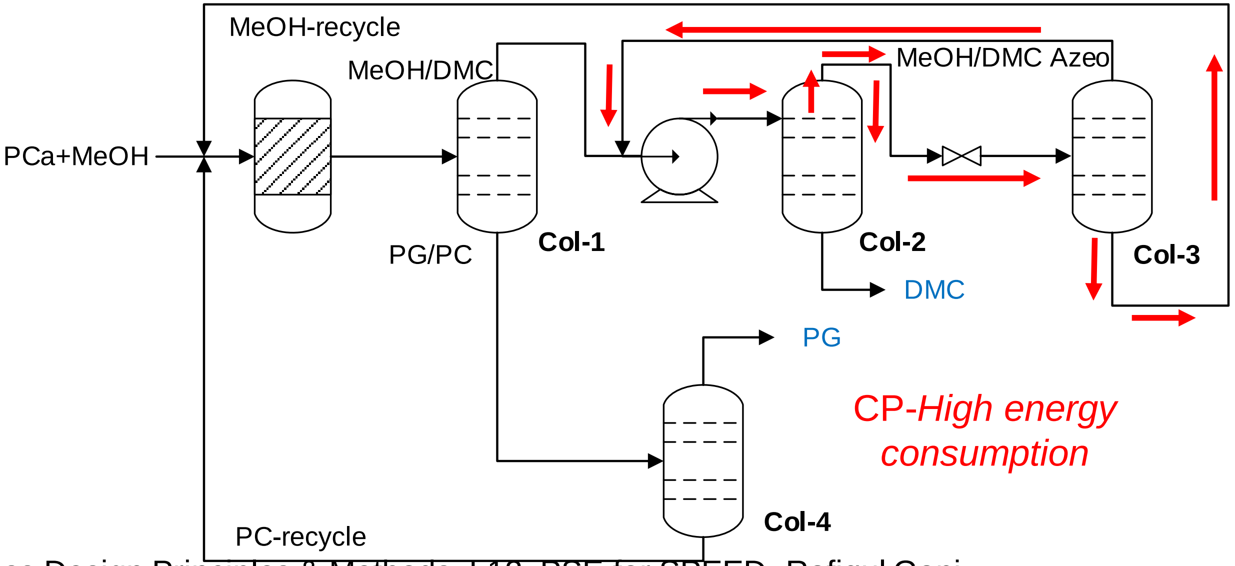

***Concept based on the BP reaction for the production of MeOAc***

# Application: Production of Di-Methyl Carbonate

- Problem Definition: The identification of intensified flowsheet alternatives for the production of *di-methyl carbonate* (DMC)
  - Reaction (liquid phase): PCa+2MeOH↔DMC+PG
- Fobj:

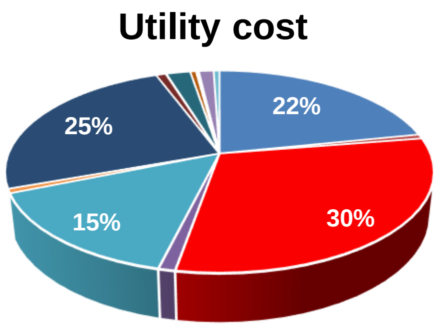
$$\mathrm{Min}\,F_{obj} = \left( E_i C_{Ut,i} + \frac{C_{Equip}}{t_{proj}} \right) \Big/ m_{prod}$$

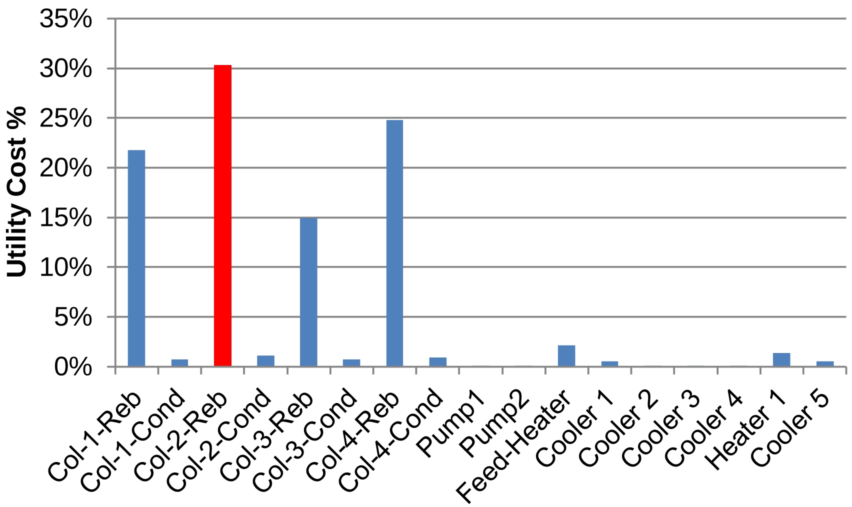
- Base Case Design:
- Sustainability Analysis

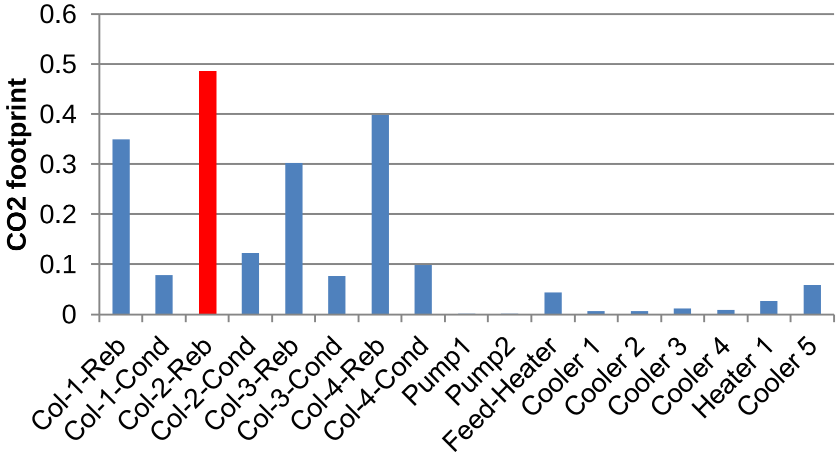



CP-*High energy consumption*

## Process *hot-spots* & *targets*




Economic, Sustainability, LCA:

1. ↑ Utility cost ↑ Energy Demand
2. ↑ Energy Demand ↑ EWC in CP
3. ↑ Energy Demand ↑ $CO_2$ footprint

Targets (e.g.):

1. Reduce energy demand
2. Reduce number of Unit-Ops
3. Explore the possibility for using ''hybrid'' Unit-Ops
4. Improve Sustainability & LCA factors

## Process Analysis:

- Thermodynamic insights
- Pure component and mixture properties
- Tasks (already known)→ phenomena

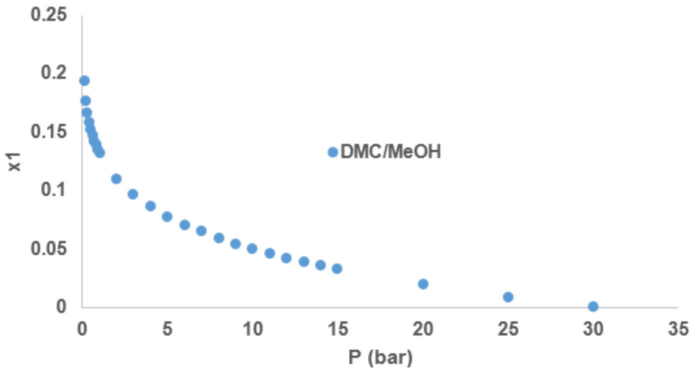
*Excerpt* of properties used for the generation of the binary ratio matrix

| $r_{ij}$ | Tb | RG | SolPar | VM |
|---|---|---|---|---|
| MeOH/PC | 1.52 | 2.2 | 1.13 | 2.1 |
| MeOH/DMC | 1.08 | 2.09 | 1.46 | 2.09 |
| MeOH/PG | 1.36 | 2.03 | 1 | 1.82 |
| PC/DMC | 1.42 | 1.05 | 1.3 | 1.01 |
| PC/PG | 1.12 | 1.08 | 1.12 | 1.16 |
| DMC/PG | 1.27 | 1.03 | 1.46 | 1.15 |

***Tb*** *-normal boiling point*
***RG*** *-radius of gyration*
***SolPar*** *-Solubility parameter*
***VM*** *-molar volume*

Hints separation based on molecular size possible

| Task | Component | PBBs |
|---|---|---|
| R-Task | PCa+MeOH | M,R,C |
| S-Task-1 | $PG_{LK}$+$PCa_{HK}$ | M,2phM,H,C,PC,PT,PS by VL |
| S-Task-2 | $MeOH_{LK}$+$PG_{HK}$ | M,2phM,H,C,PC,PT,PS by VL |
| S-Task-3 | $MeOH_{LK}$+$DMC_{HK}$ | M,2phM,H,C,PC,PT,PS by VL |
| LK-Light key<br>HK-Heavy key | | |

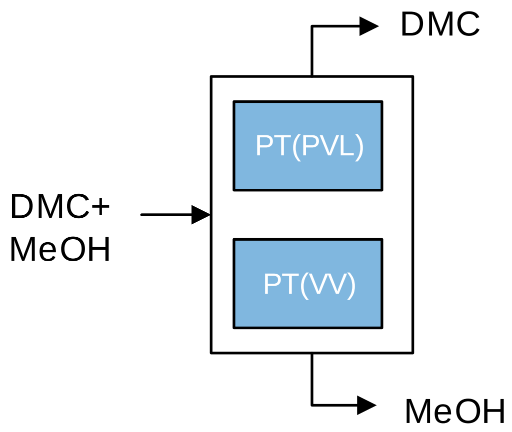


## Identification of tasks and PBBs:

- Example, S-Task-3: Separation of MeOH/DMC azeotrope
- Identify PBBs which fulfill the task in multiple ways
- Identified PBBs search space:
  - R, $M_I$, $M_{FL}$, $M_R$ $M_V$, 2phM, PC(VL), PT(VL), PT(PVL), PT(VV), PS (VL), PS(VV), D, H, C-15 in total
  - All possible combinations- 16278
  - Reduced to 64-combination rules
    - PC(VL)↔PT(VL): *M=2phM=PC(VL)=PT(VL)*: S-Task
    - R↔PT(VL): *M=R=2phM=PC(VL)=PT(VL)=PS(VL)*: R-S Task

  *that is merged R-Task and S-Task*

*Thermodynamic insights*




*Represents separation through a membrane*

## SPBs

M(L)=R(L)

M(L)=2phM=PC(VL)=PT(PVL)=PS(VL)

M(VL)=2phM=R=PC(VL)=PT(VL)=PS(VL)

M(V)=2phM=PT(VV)=PS(VV)

## Basic Structures

M(L)=R(L)=C

M(VL)=2phM
M(L)=2phM=PC(VL)=PT(PVL)=PS(VL)
M(V)=C

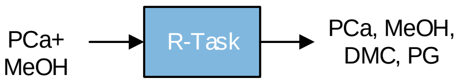
M(VL)=2phM
M(V)=2phM=PC(VL)=PT(VV)=PS(VV)
M(L)=H

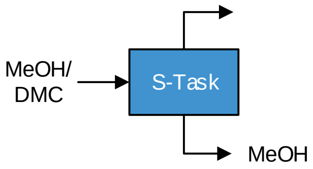
M(VL)=C=2phM=PC(VL)=PT(VL)=PS(VL)
M(VL)=2phM=PC(VL)=PT(VL)=PS(VL)
M(VL)=H=2phM=PC(VL)=PT(VL)=PS(VL)

**Note:** The objective is to convert input (PCa + MeOH) to output( DMC + PG). One basic structure (unless combined) will not achieve this

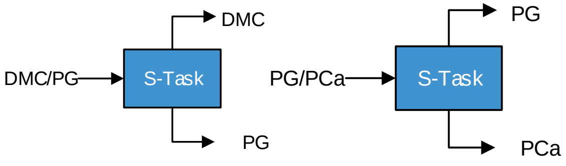
**Note:** This basic structure fulfills two S-tasks

## Task fulfilled

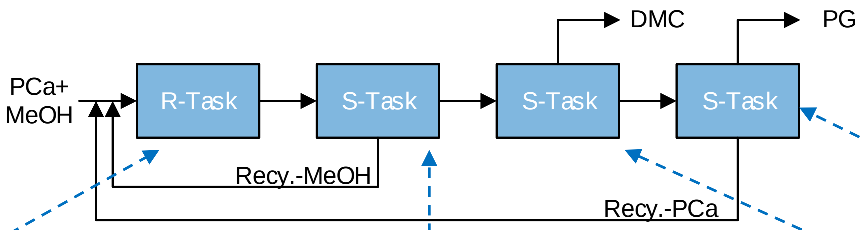



**Note:** This task can be performed in multiple ways using 2 basic structures




## Flowsheet alternative



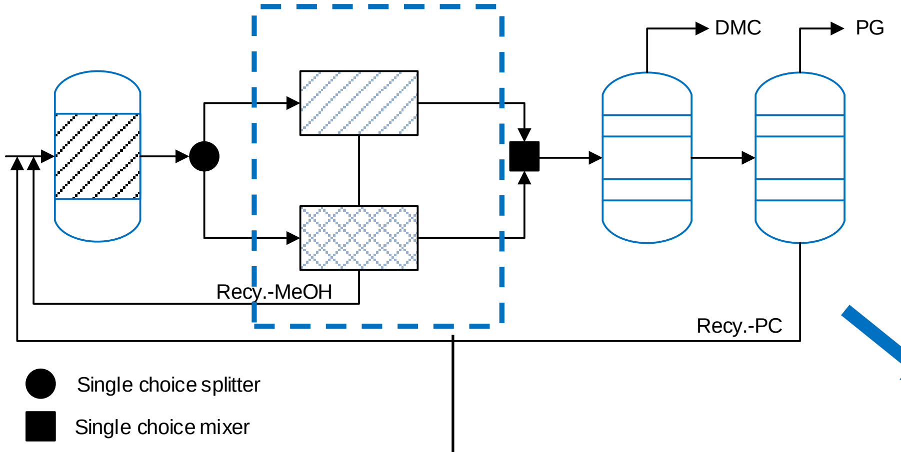

Change of state of raw materials, a reaction task is identified

Azeotrope DMC/MeOH, removal of MeOH is beneficial

Separation between PG/PCa is feasible

Separation between DMC/PG is feasible

## The flowsheet alternative based on the task diagram

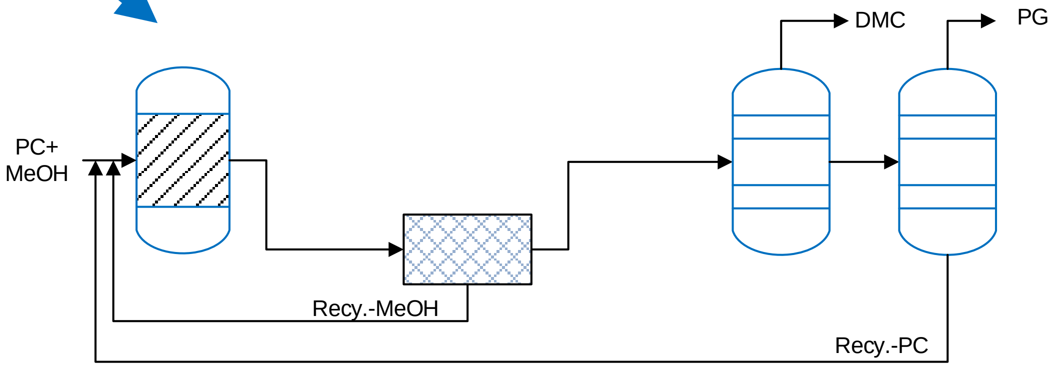



[Option:](#) Which membrane to be used?

[Choice:](#)

-Available membrane: *vapor permeation*

-Availability of data

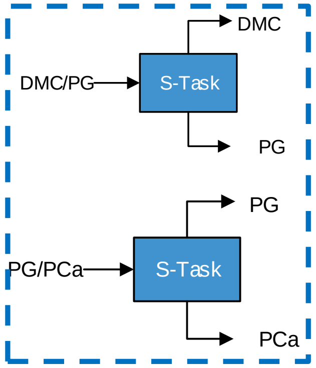



Flowsheet Alternative 2

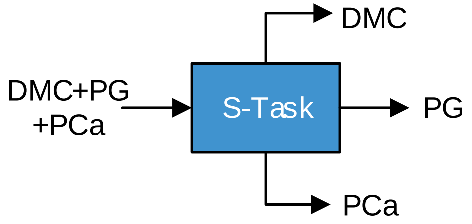
***Recall:***

| |
|---|
| M(VL)=C=2phM=PC(VL)=PT(VL)=PS(VL) |
| M(VL)=2phM=PC(VL)=PT(VL)=PS(VL) |
| M(VL)=H=2phM=PC(VL)=PT(VL)=PS(VL) |

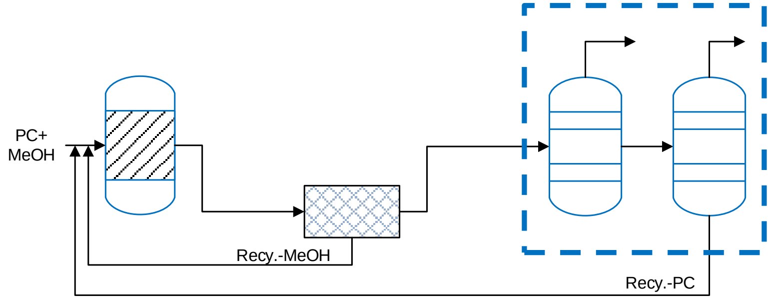
This basic structure fulfills two S-tasks



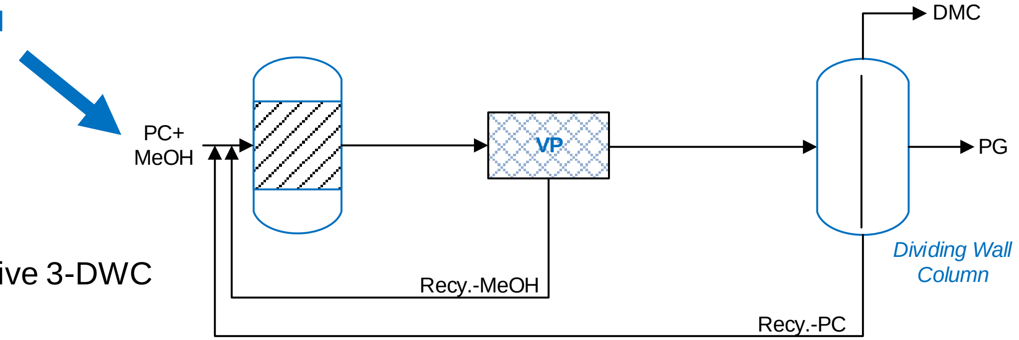

Tasks can be merged




Properties:
-Same basic structure
-No azeotropes present
-Distinct TBP




Separation combined




Flowsheet Alternative 3-DWC

***Recall:***

| |
|---|
| M(L)=R(L) |
| M(L)=C |

| |
|---|
| M(VL)=2phM |
| M(V)=2phM=PC(VL)=PT(VV)=PS(VV) |
| M(L)=H |

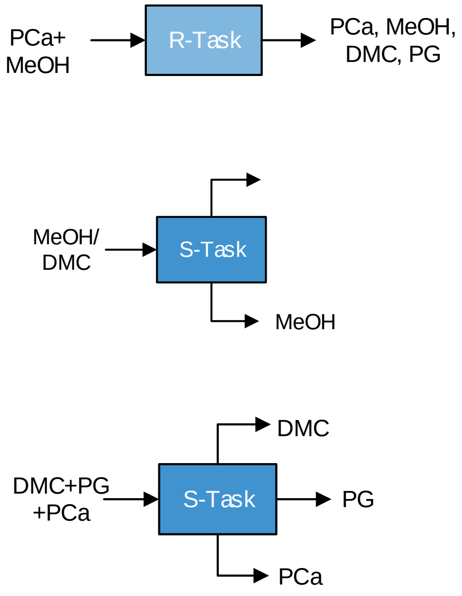
| |
|---|
| M(VL)=C=2phM=PC(VL)=PT(VL)=PS(VL) |
| M(VL)=2phM=PC(VL)=PT(VL)=PS(VL) |
| M(VL)=H=2phM=PC(VL)=PT(VL)=PS(VL) |

Consider: Can reaction and separation be combined?

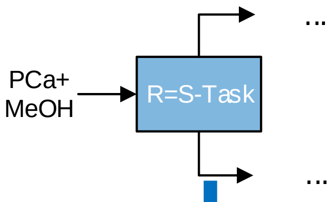
| |
|---|
| M(VL)=C=2phM=PC(VL)=PT(VL)=PS(VL) |
| M(VL)=R=2phM=PC(VL)=PT(VL)=PS(VL) |
| M(VL)=H=2phM=PC(VL)=PT(VL)=PS(VL) |

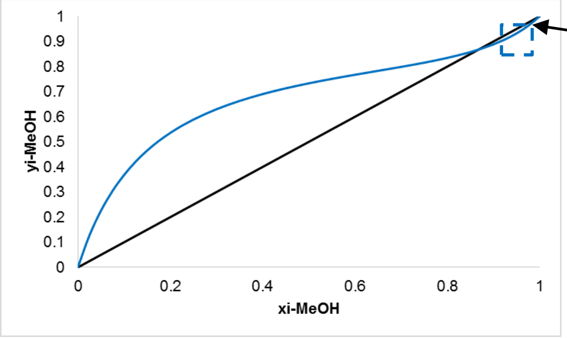
Properties:
- -Equilibrium reaction
- -Esterification reaction
- -Liquid phase reaction
- -Azeotropes present

Basic structures are combined

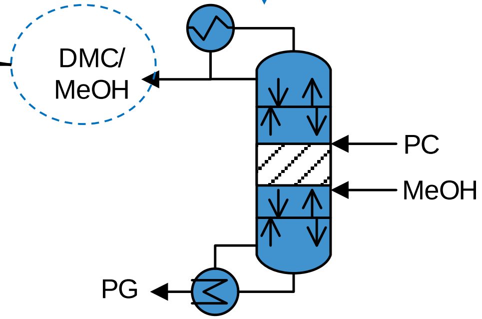



Tasks are merged




How to obtain pure DMC?



## Basic Structure

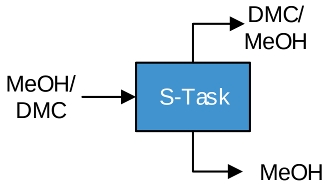
*S-phase-V, Azeo-Yes, Feed Cond.-V*

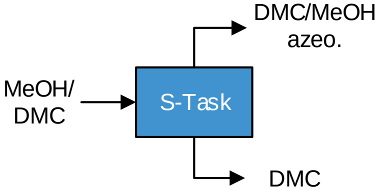
| |
|---|
| M(V)=2phM |
| M(V)=2phM=PT(VV)=PS(VV) |

*S-phase-VL, Azeo-Yes, Feed Cond.-VL*

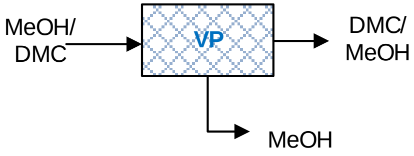
| |
|---|
| M(VL)=C=2phM=PC(VL)=PT(VL)=PS(VL) |
| M(VL)=2phM=PC(VL)=PT(VL)=PS(VL) |
| M(VL)=H=2phM=PC(VL)=PT(VL)=PS(VL) |

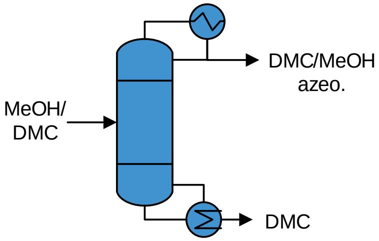
## Task fulfilled

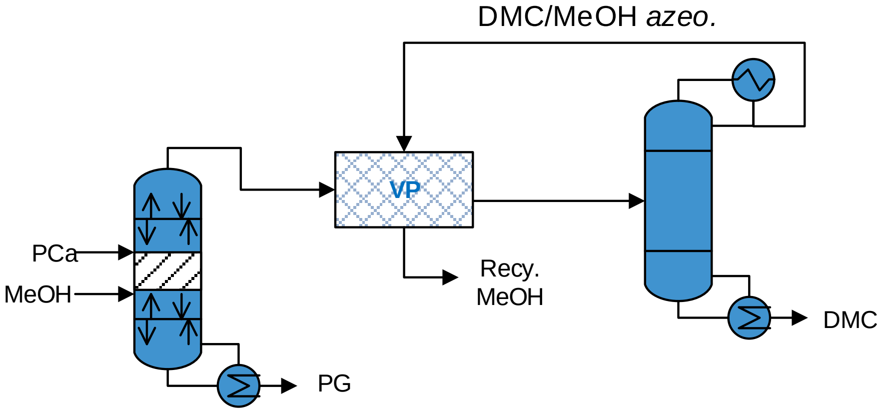



## Unit-Op




Flowsheet Alternative 4-RD

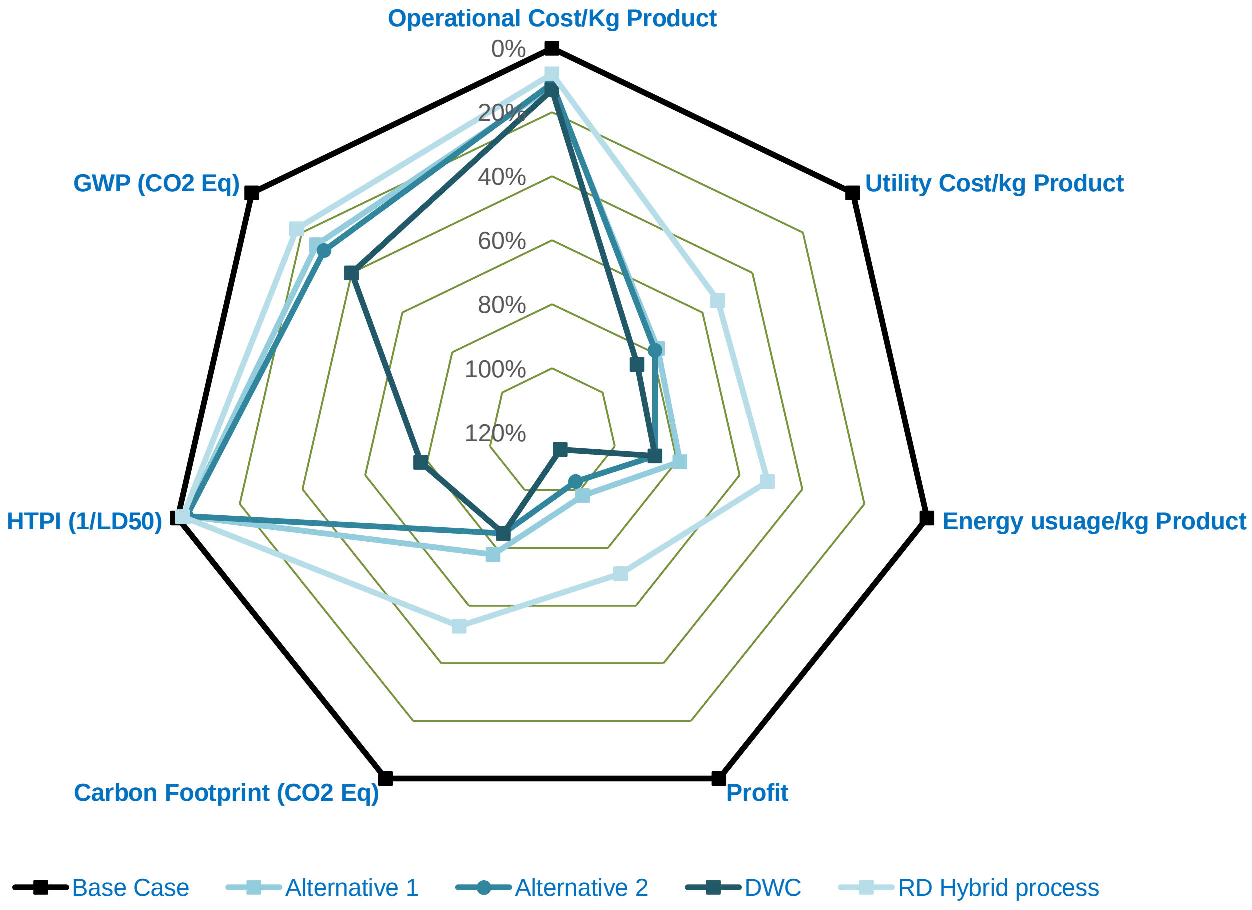
## Sustainability Analysis: comparison of alternatives

| Primary Performance Metric | Design | | | | |
|---|---|---|---|---|---|
| | Base Case | Alternative 1 | Alternative 2 | DWC | RD |
| *Energy Usage/kg DMC* | 78.65 | 16.74 | 10.47 | 10.44 | 38.17 |
| *Utility Cost/kg DMC* | 0.36 | 0.08 | 0.05 | 0.05 | 0.16 |
| *RM Cost/kg DMC* | 2.03 | 2.03 | 2.04 | 2.03 | 2.03 |
| *Profit/kg DMC* | 0.27 | 0.54 | 0.55 | **0.58** | 0.47 |
| *TAC/kg DMC (Fobj)* | 0.36 | 0.08 | 0.09 | **0.06** | 0.18 |

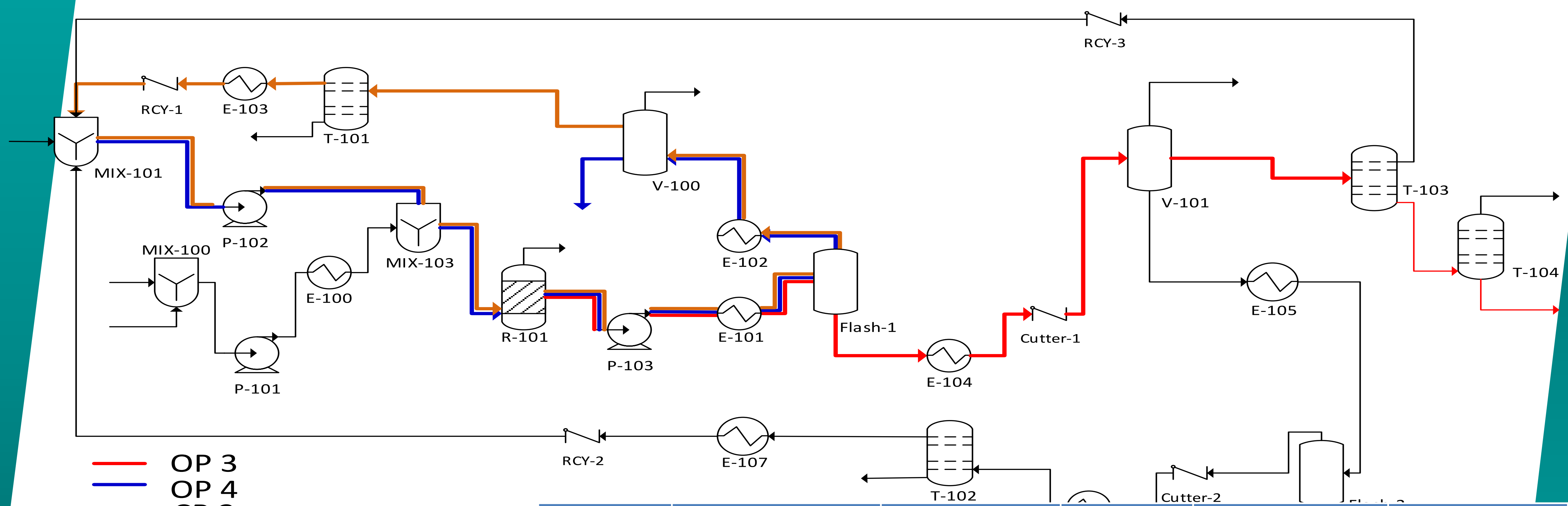
- Recall Targets
  - Reduce energy demand-Yes
  - Reduce number of Unit-Ops-Yes
    - Base Case = **5**, Alternative 2 = 4 DWC = **3**, RD = **3**
  - Explore the possibility for using ‘’hybrid’’ Unit-Ops-Yes
  - Improve Sustainability & LCA factors-Yes

- ***TARGETS HAVE BEEN MET***

■ Global Picture

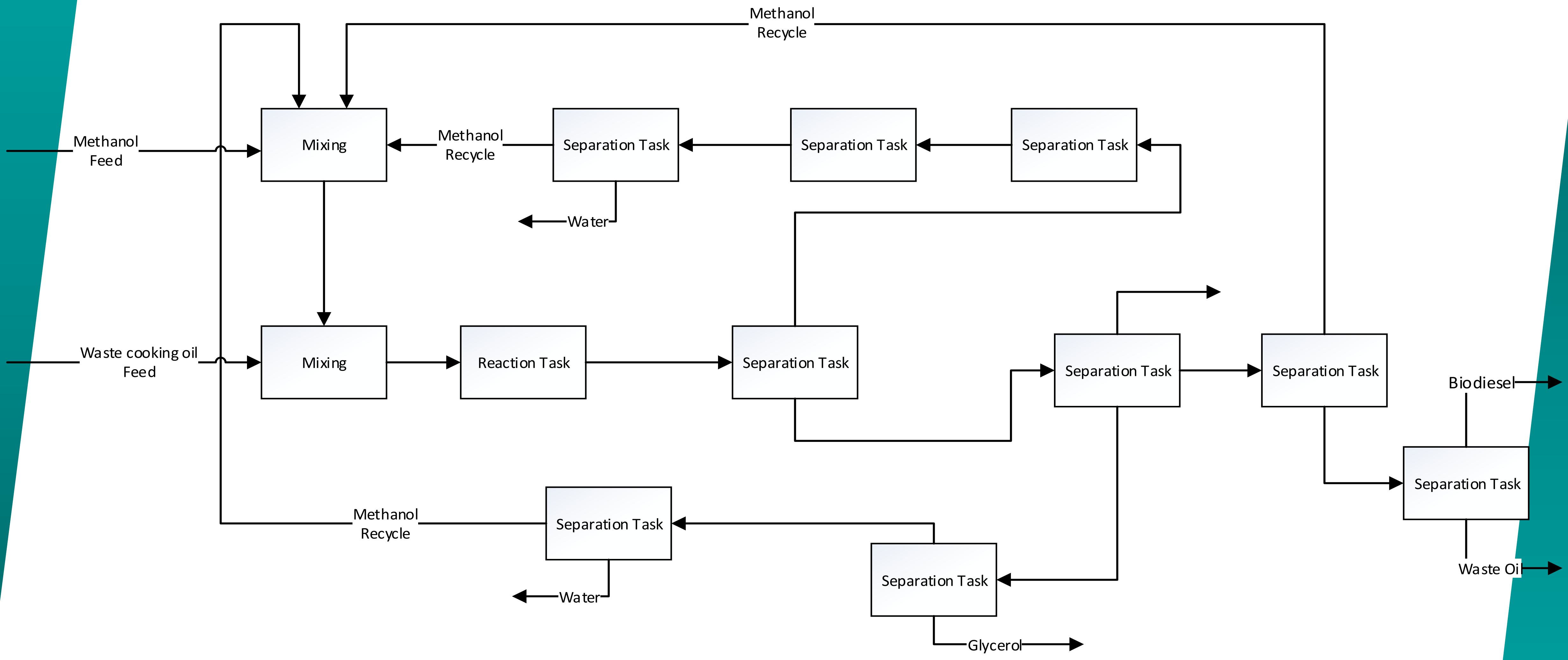


# Stage 3: Targeted process improvement (Biodiesel)

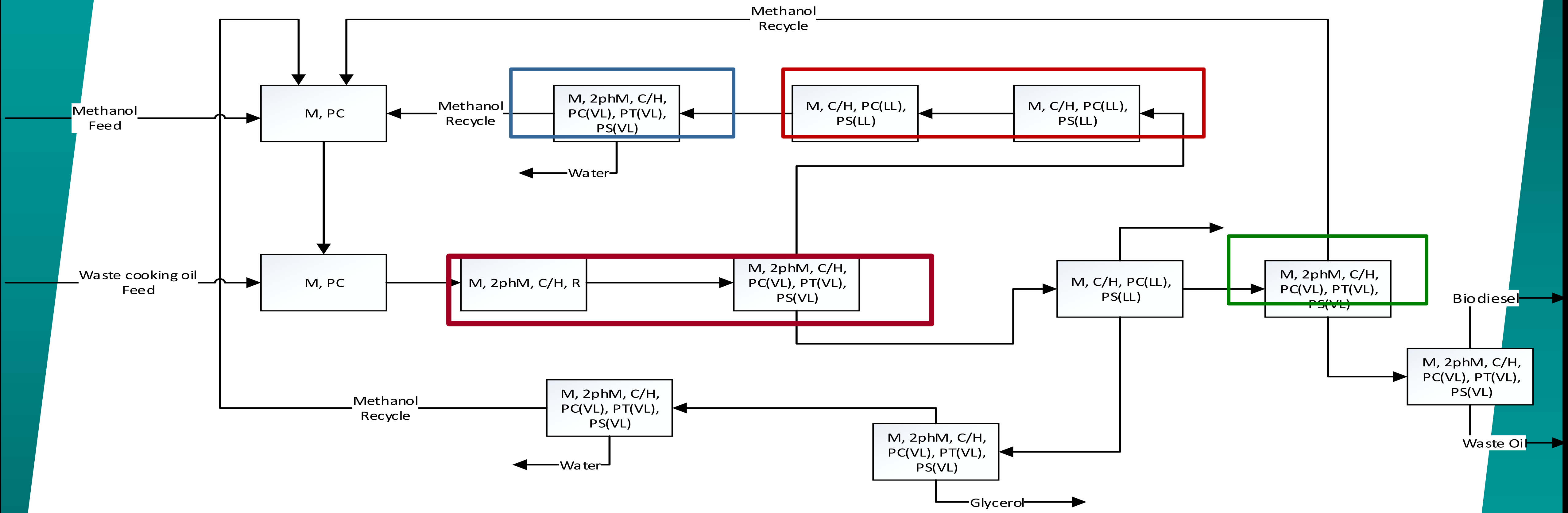



| Path | MVA | Probability | Path | TVA | Probability |
|---|---|---|---|---|---|
| **OP3** | –14174.30098 | High | OP3 | –14898.0917 | High |
| **OP4** | –2047.234859 | High | - | - | - |
| **C 2** | 496.6545095 | High | C2 | 496.6545095 | High |

# Biodiesel production: Identify tasks

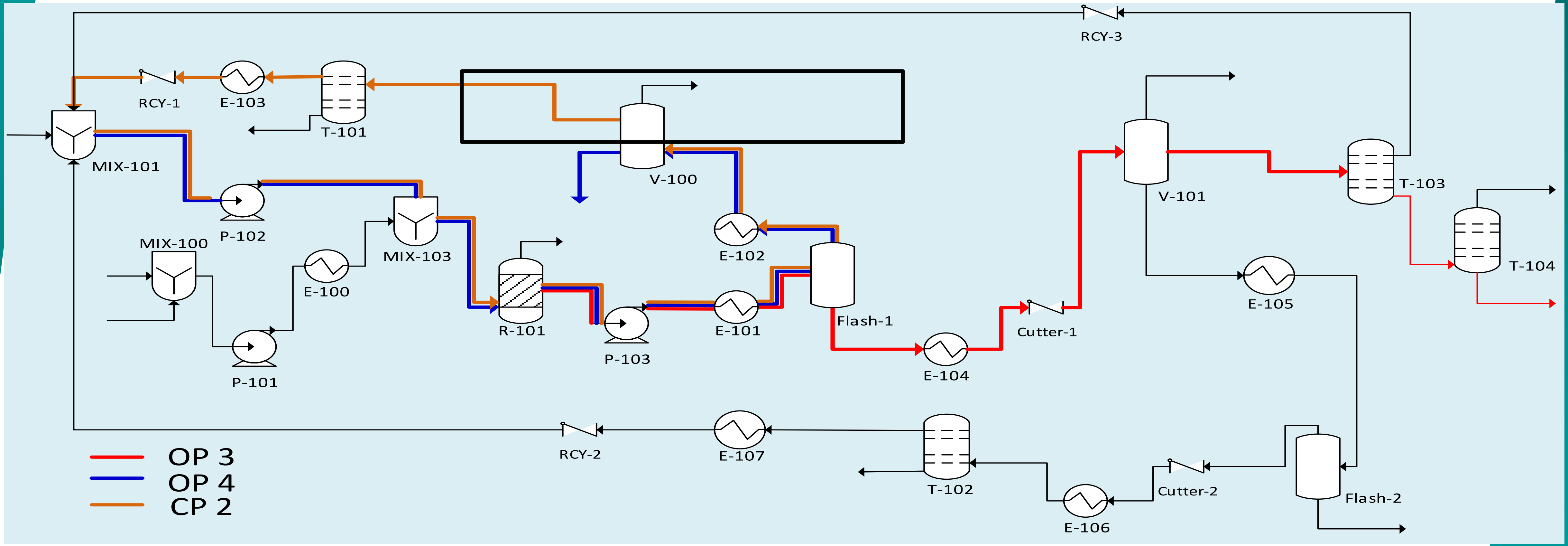


# Biodiesel production: Identify phenomena



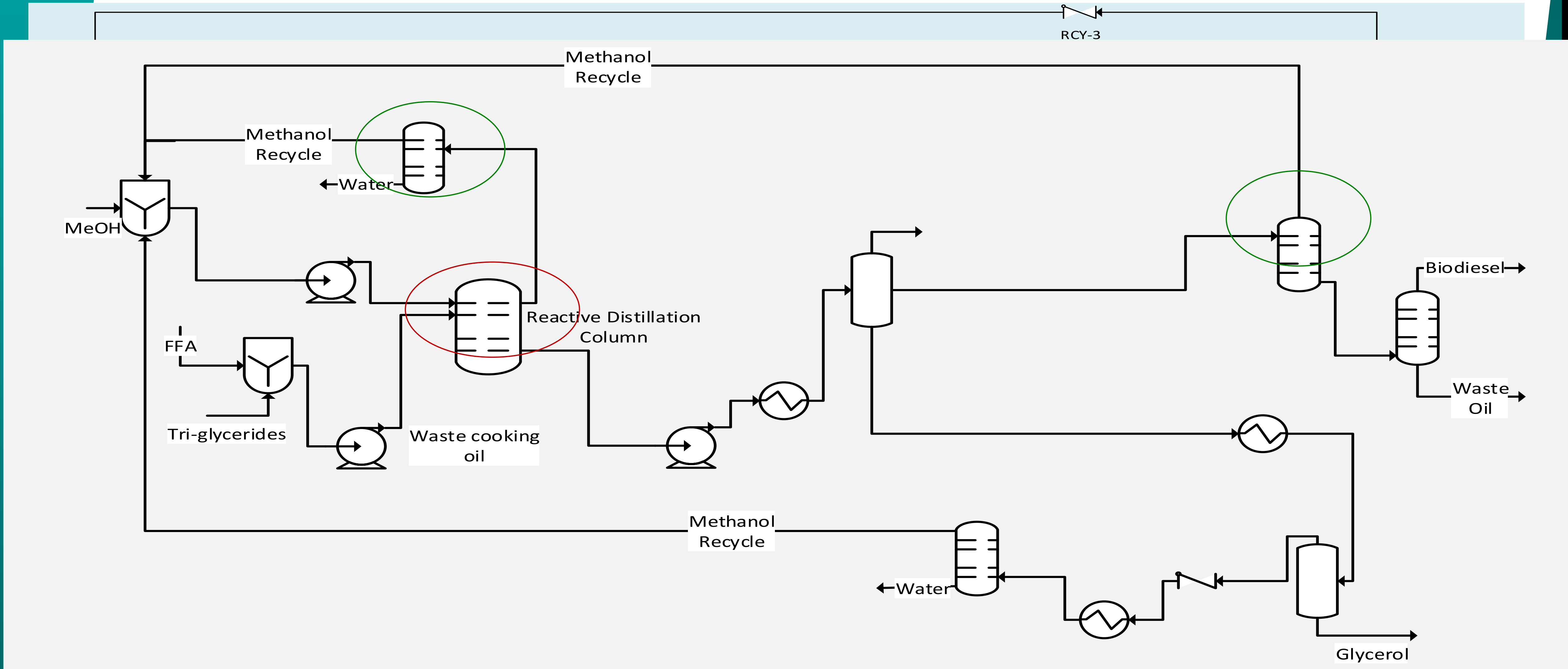

**Mansouri et al. 2013**

# Identify more sustainable (PI) solutions



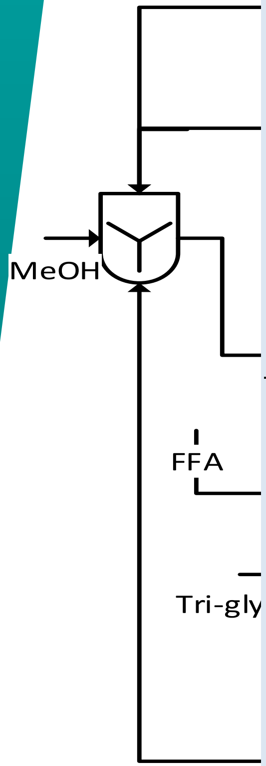

**Mansouri et al. 2013**

# Identify more sustainable (PI) solutions




**Mansouri et al. 2013**

# Compare more sustainable (PI) alternatives



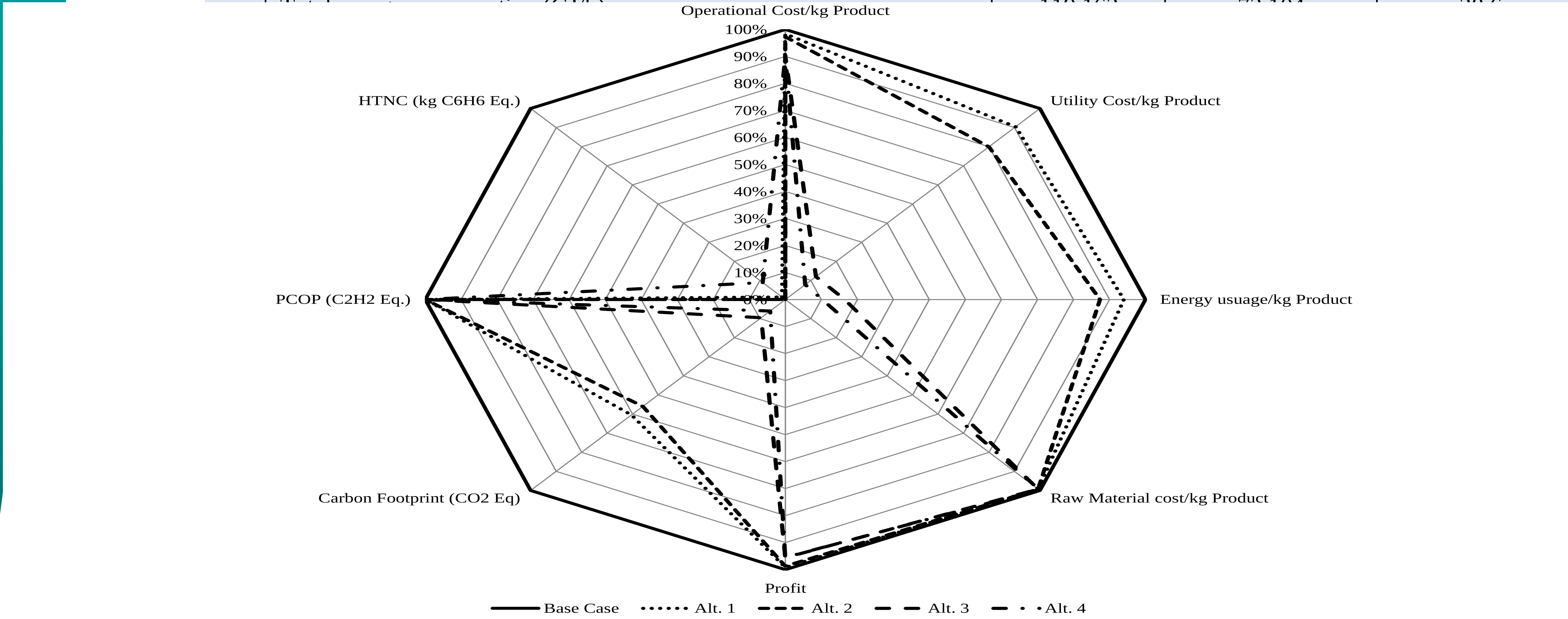

| | Sustainability Metrics | Base case design | Intensified alternative | %Improvement |
|---|---|---|---|---|
| Performance metrics | Total utility cost (\$/year) | 7,790,000 | 4,660,000 | 40.2 |
| | Total energy consumption (GJ/h) | 119.163 | 73.104 | 38.6 |
| | product/raw material (kg/kg) | 0.94 | 0.94 | 0 |
| | Energy/ products (GJ/kg) | 0.0025 | 0.0017 | 32 |
| | Net water added to the system ($m^3$) | 0 | 0 | 0 |
| | Water for cooling/product ($m^3$/kg) | 0.017 | 0.017 | 0 |
| | Waste/raw material (kg/kg) | 0.032 | 0.026 | 18.8 |
| | Waste/products (kg/kg) | 0.034 | 0.028 | 17.6 |
| | Hazardous raw material/product (kg/kg) | 0 | 0 | 0 |
| | Number of unit operations | 9 | 7 | 22 |
| LCA | Total carbon footprint (kg $CO_2$ eq.) | 0.183 | 0.143 | 21.8 |
| | HTPI - Human Toxicity Potential by Ingestion ($1/LD_{50}$) | 0.51811 | 0.51111 | 0 |
| | HTPE - Human Toxicity Potential by Exposure ($mg_{emiaaion}/m^3$) | 0.03558 | 0.03564 | 0 |
| | GWP - Global Warming Potential ($CO_2$ eq.) | 0.55214 | 0.55241 | 0 |
| | ODP - Ozone Depletion Potential (CFC-11 eq.) | 5.18E–09 | 5.18E–09 | 0 |
| | PCOP - Photochemical Oxidation Potential ($C_2H_2$ eq.) | 0.04968 | 0.04976 | 0 |
| | AP - Acidification Potential ($H^+$ eq.) | 0.00010 | 0.00010 | 0 |
| | ATP - Aquatic Toxicity Potential ($1/LC_{50}$) | 0.00366 | 0.00366 | 0 |
| | TTP - Terrestrial Toxicity Potential ($1/LD_{50}$) | 0.51811 | 0.51111 | 0 |
| | HTC (Benzene eq.) - human toxicity (carcinogenic impacts) | 2062.7 | 1794.5 | 13 |
| | HTNC (Toluene eq.) - human toxicity (non-carcinogenic impacts) | 1.3301 | 1.1795 | 11.3 |
| | ET (2, 4-D eq.) - Fresh water ecotoxicity | 0.00525 | 0.00490 | 6.7 |

$LC_{50}$ is lethal concentration ($mg_{emission}/kg_{fathead\ minnow}$)
$LD_{50}$ is one kg body weight of rat administered in milligrams of toxic chemical by mouth ($mg_{emission}/kg_{rat}$)

**Mansouri et al**

# Compare more sustainable (PI) alternatives

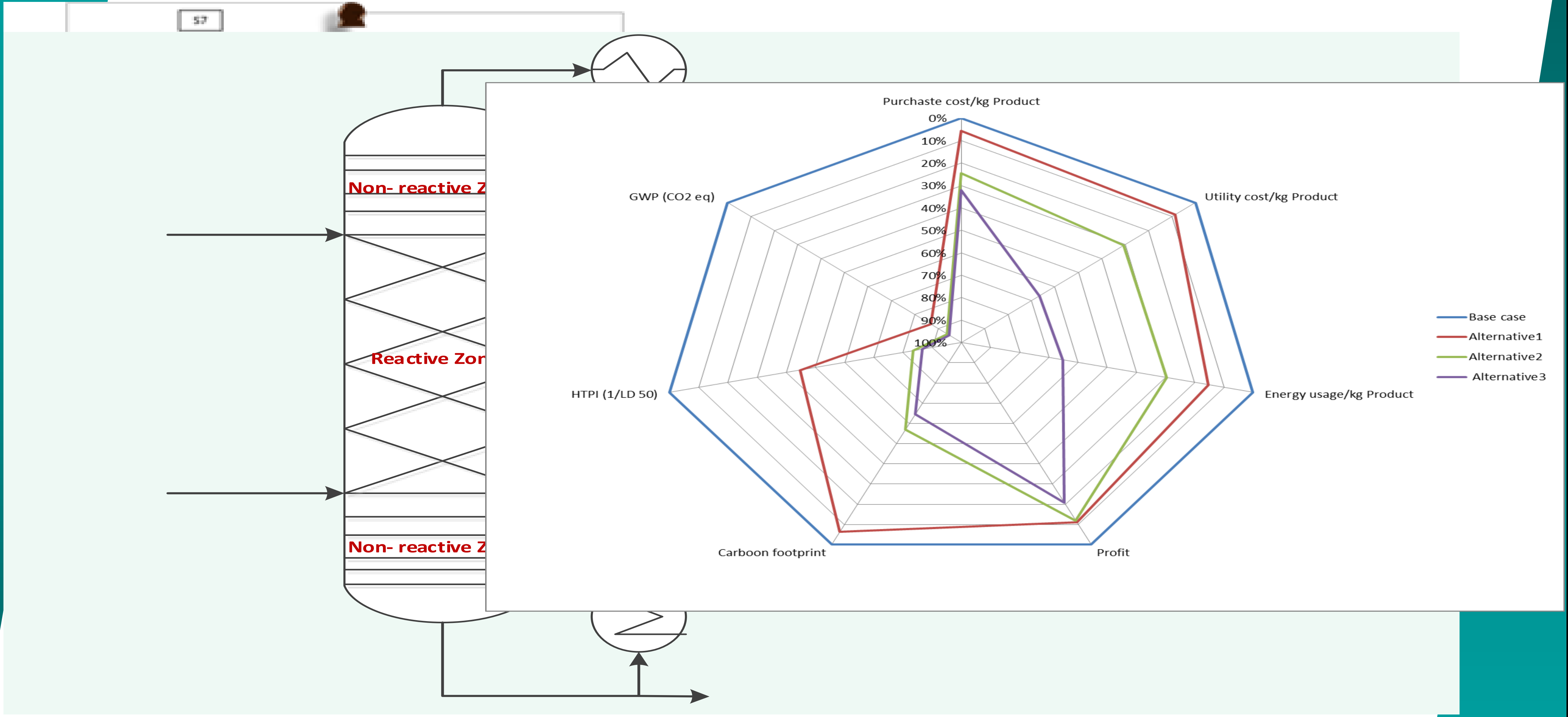
| | Sustainability Metrics | Base case design | Intensified alternative | %Improvement |
|---|---|---|---|---|
| | Total utility cost ($/year) | 7,790,000 | 4,660,000 | 40.2 |



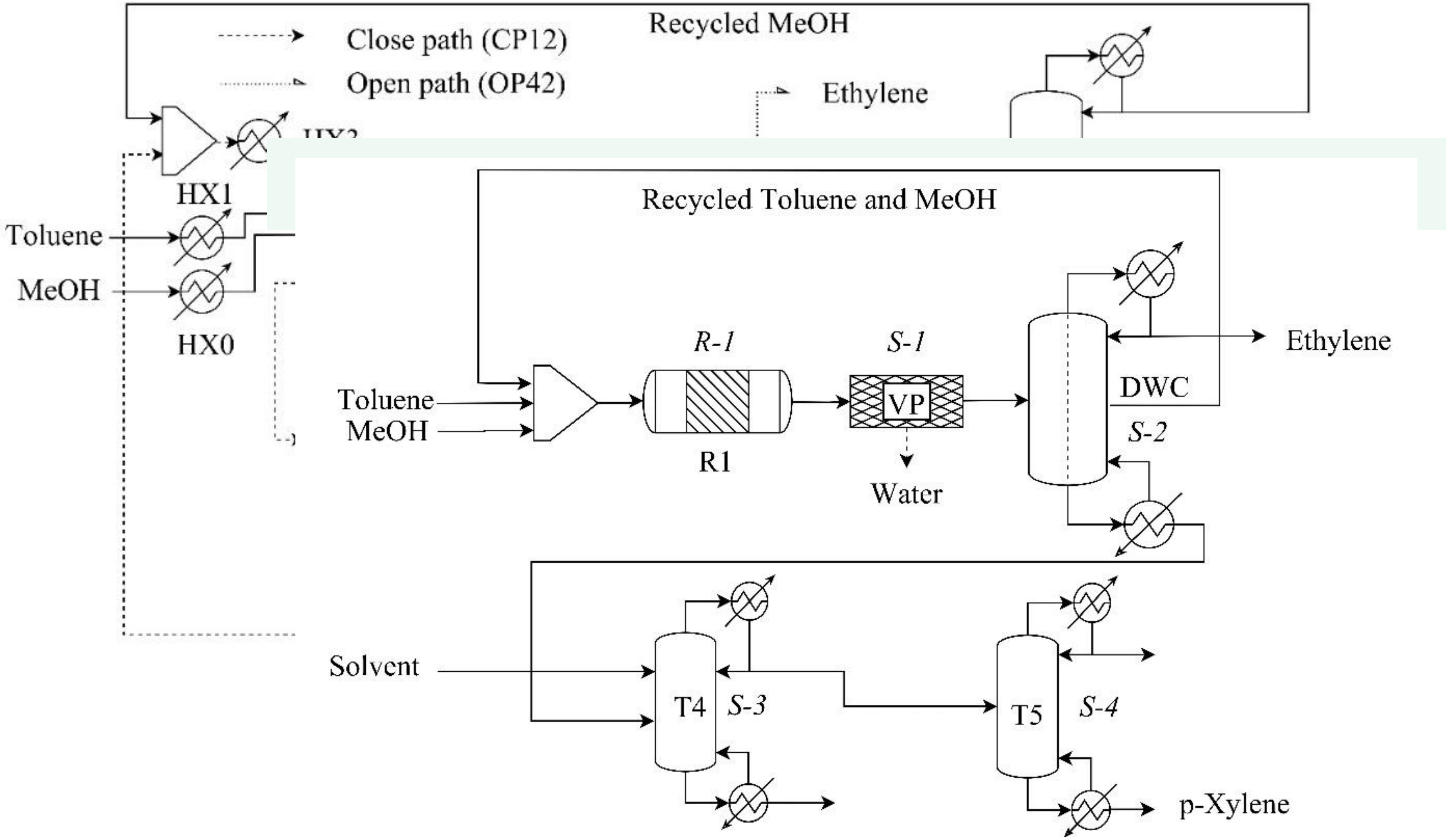

$LD_{50}$ is one kg body weight of rat administered in milligrams of toxic chemical by mouth ($mg_{emission}/kg_{rat}$)

**Mansouri et al**

# More examples (synthesis of dioxolane products)



# More examples (toluene to p-xylene)




Anantasarn et al, CACE 2017 (PI Special Issue)

# Conclusions

- A computer-aided systematic *multi-level* framework for performing process synthesis inclusive of process intensification and for generating more sustainable designs has been presented
- The concept of phenomena based PI is promising because it has been shown that feasible intensified flowsheet alternatives are generated at this lower scale
- The framework has been successfully applied to 3 case studies and more sustainable designs having non-trade of solutions have been obtained
  - Methyl-acetate: *a total of 9 alternatives have been generated of which 4 are better compared to the base case design of which a novel design compared to the well-known reactive distillation has been found*
  - Di-methyl Carbonate: *a total of 9 alternatives have been generated of which 4 are better compared to the base case design*