Achieving more sustainable solutions through process intensification

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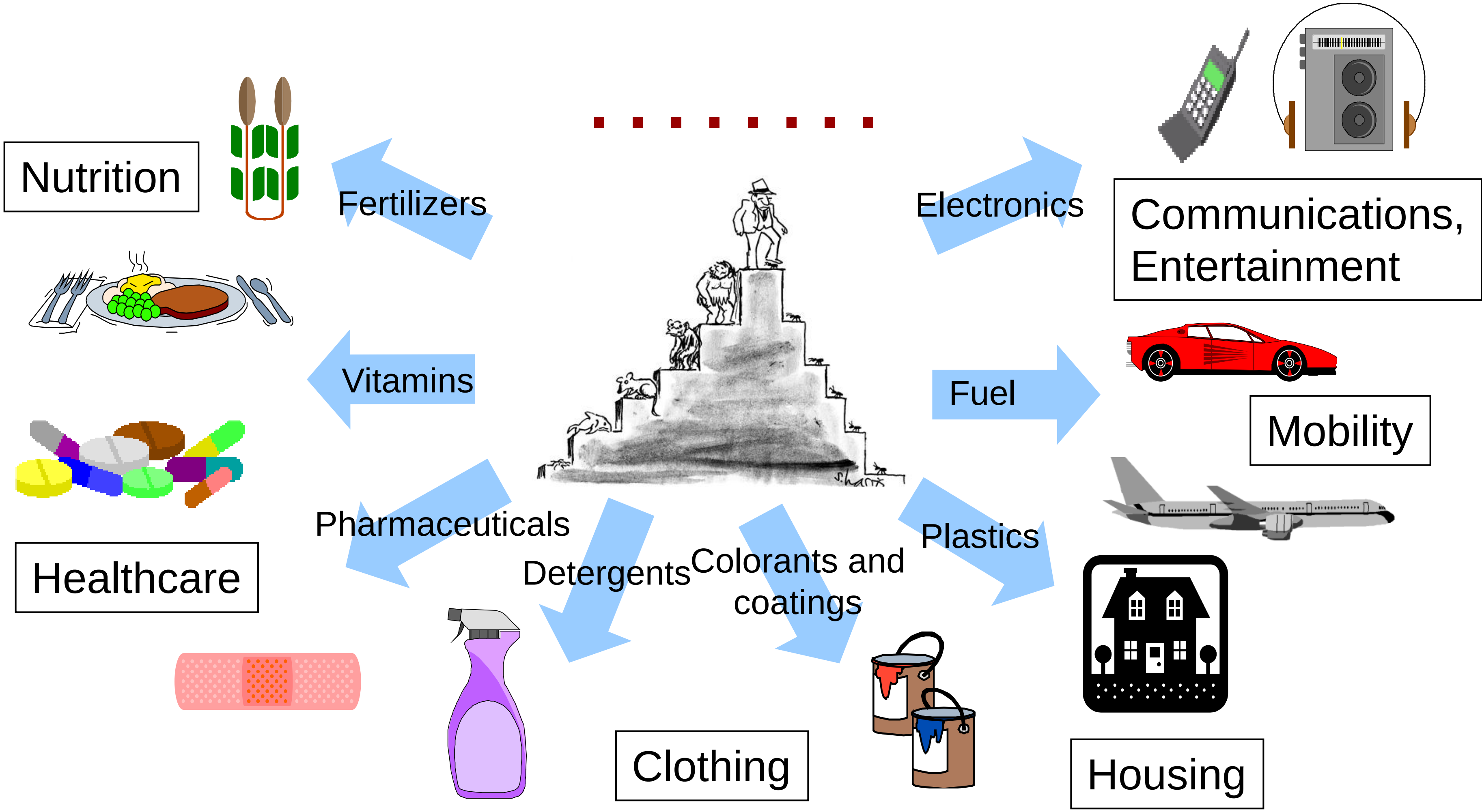
***Sustainable product-process engineering, evaluation & design**

Master of the planet earth – how did we get there?

Positive contribution to the modern society



Nutrition

Fertilizers

Electronics

Communications, Entertainment

Vitamins

Fuel

Mobility

Pharmaceuticals

Healthcare

Detergents

Colorants and coatings

Plastics

Clothing

Housing

Survival of the modern society depends on the products from ChE

Is our future sustainable?

The future scenario

- **World population stabilizing at 9-10 billion**
- **6-7 X world GDP growth over next 50 or so years (in constant dollars)**
- **5-6 X existing production capacity for most commodities (steel, chemicals, lumber, etc.)**
- **3.5 X increase in energy demand (7X increase in electricity demand)**
- **Increase in water demand**
- **Costs related to CO_2 emissions (7 GTC/yr to 26 GTC/yr)**

Siirola, PSE-2012

Is our future sustainable? - motivation

Convert raw materials to products

↓

Use resources (energy, water, ….)

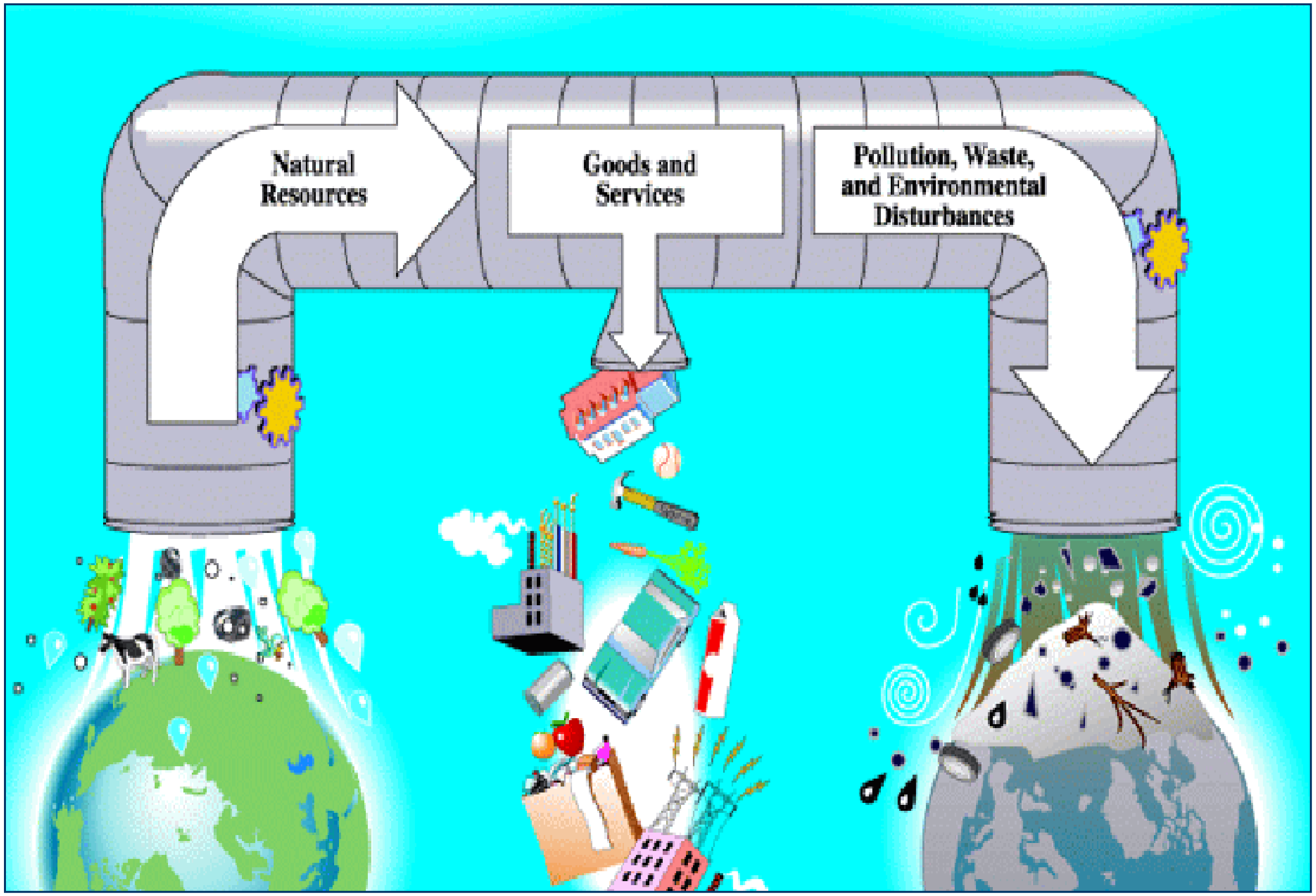
↓

Environmental Impacts (GWP, OD, HTTP, …)

↓

Produce waste

The challenges facing us



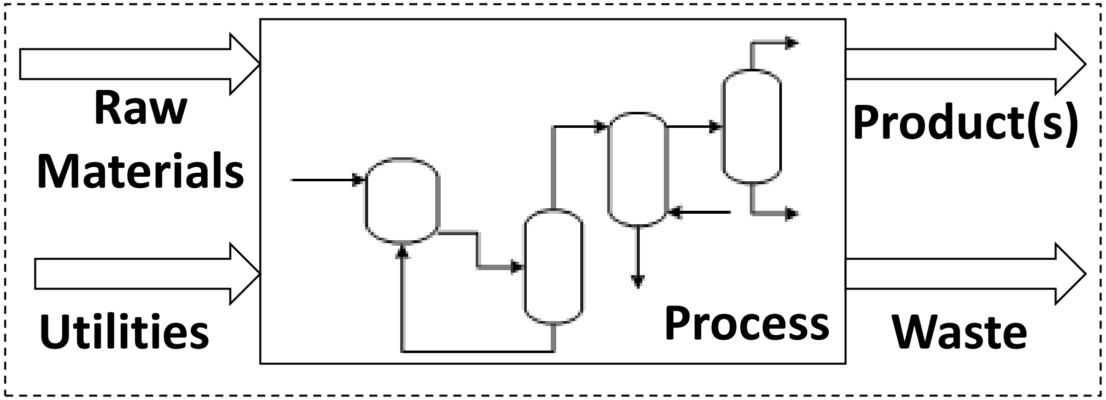
Only 25% converted; must be > 40% (Driolli 2007)

The synthesis/design problem

Chemical and bio-based engineering community faces enormous challenges to address the issues

Establish sustainable production

Adopt to changing markets



Raw Materials

Utilities

Process

Product(s)

Waste

Survive global competition

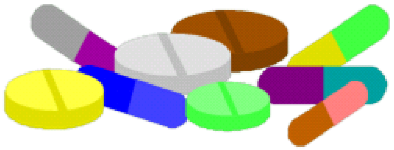
Demands for innovative products & processes

Needed: Innovative and more sustainable alternatives

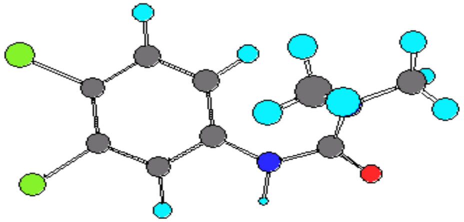
That are economically feasible; has reduced waste; utility efficient; environmentally acceptable; safe; operable; ……. (order of magnitude better)

Related questions: What? Why? How?

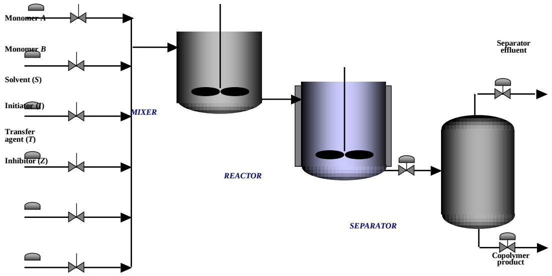
Product



Product function



Process function



Process

Refined Chemicals & Consumer Products (≈ 30000)

Plastics, pharmaceuticals, dyes, solvents, fertilizers, fibres, dispensers, cosmetics,

Intermediate Products (≈ 300)

Methanol, vinyl chloride, styrene, urea, formaldehyde, ethylene oxide, acetic acid, acrylonitrile, cyclohexane, acrylic acid

Basic Products (≈ 20)

Ethylene, propene, butadiene, benzene, synthesis-gas, actylene, ammonia, sulfuric acid, sodium hydroxide, chlorine

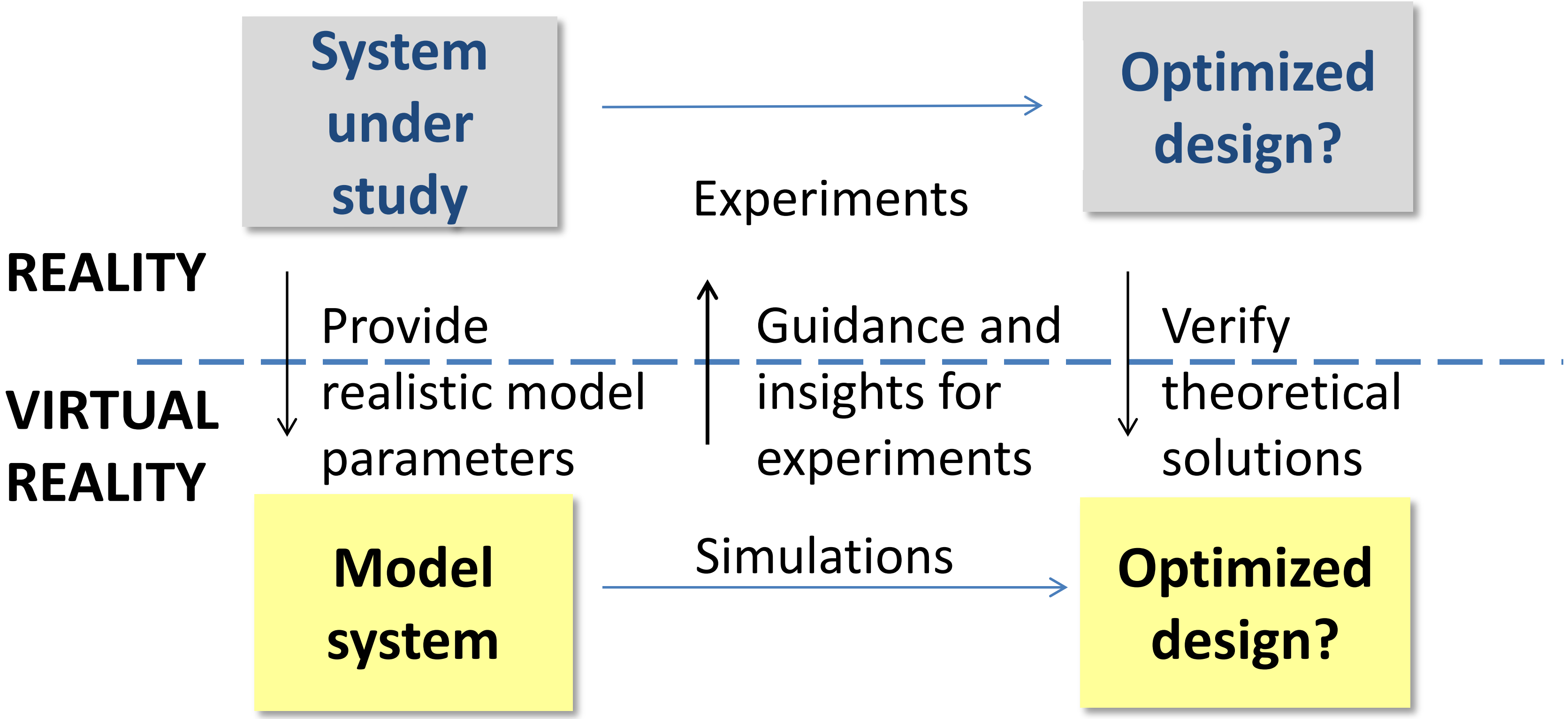
Raw Materials (≈ 10)

Petroleum, natural gas, coal, biomass
Rock, salt, phosphate, sulfur, air, water

What is the best way to identify, design, develop, ………….

the chemicals based products & their processes?

The Product-Process Design Framework



System under study

Experiments

Optimized design?

REALITY

Provide realistic model parameters

Guidance and insights for experiments

Verify theoretical solutions

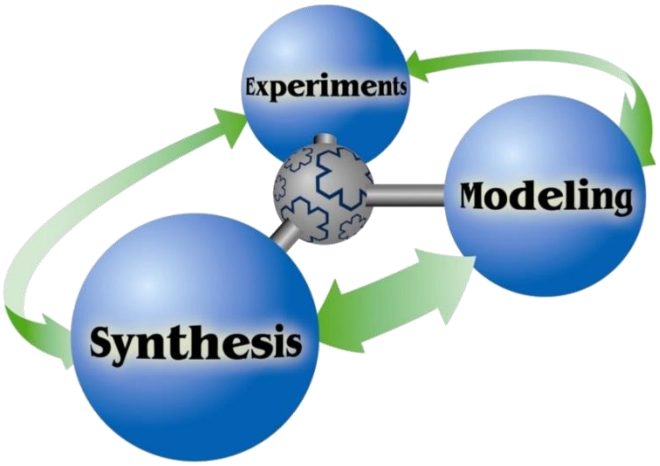
VIRTUAL REALITY

Model system

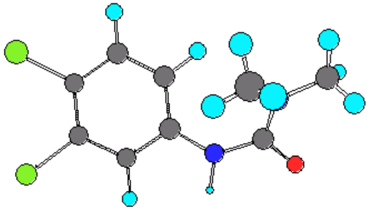
Simulations

Optimized design?

- Approaches
  - Integrated modeling, experiments and synthesis
  - Ability to find predictive-innovative solutions

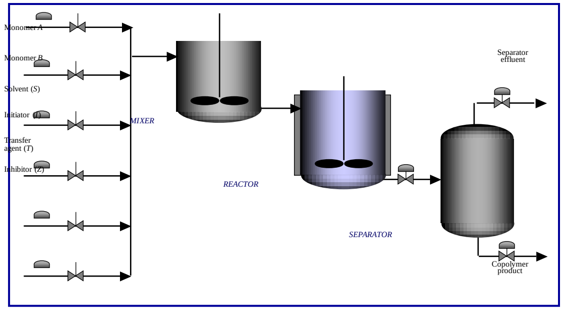


Knowledge-data-models



Property models

$$Log\ P_i = A_i + [B_i/(C_i + T)]$$



Process models

$$\frac{dm_i}{dt} = f_{in,i} - f_{out,i} - r(m,T,P)V; i = 1, NC$$

Models for environmental impact

Operation models

Process models

Property-kinetics models

Cost models

Models for sustainability metrics

Formulation process model

Product evaluation model

General mathematical problem

$\mathrm{Fobj} = \min \{C^T\underline{y} + f(\underline{x}, \underline{y}, \underline{u}, \underline{d}, \underline{\theta}) + S_e + S_i + S_s + H_c + H_p\}$ 1

Process-product model

$P = P(\underline{f}, \underline{x}, \underline{y}, \underline{d}, \underline{u}, \underline{\theta})$ 2

Process-product

$0 = h_1(\underline{x}, \underline{y})$ 3

Equipment-material

$0 \geq g_1(\underline{x}, \underline{u}, \underline{d})$ 4a

$0 \geq g_2(\underline{x}, \underline{y})$ 4b

Flowhseet-chemical alternatives

$B\,\underline{x} + C^T\underline{y} \geq D$ 5

Problems:

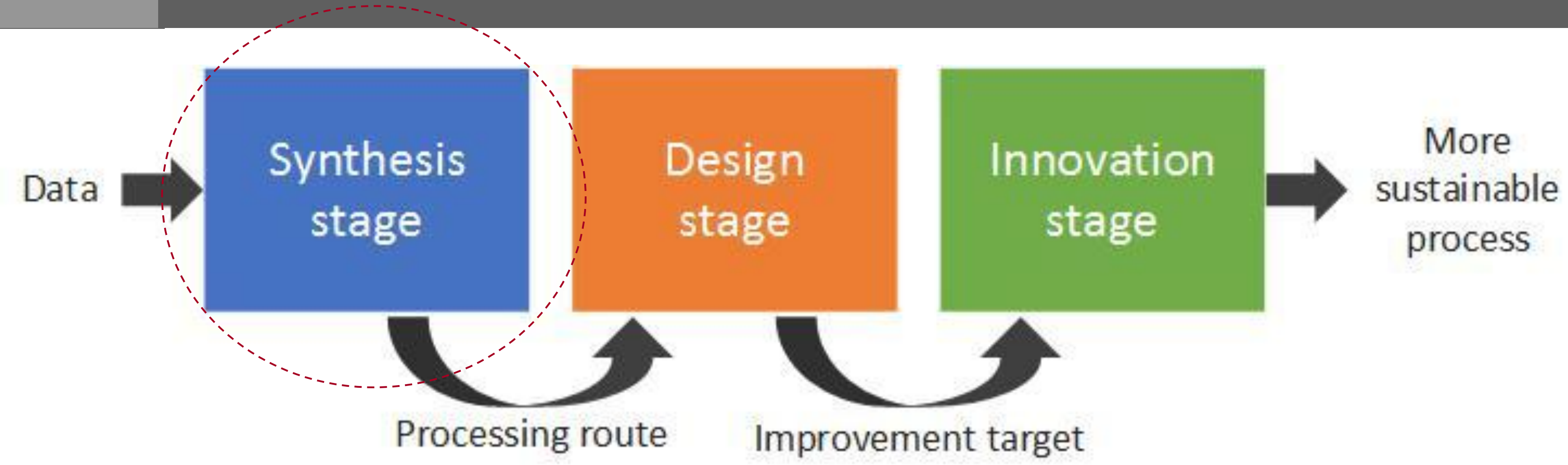
LP, NLP, MILP, MINLP, process simulation, ...

Solution strategies:

Direct,
Decomposition based

$\underline{x}$: real-process variables; $\underline{y}$ integer-decision variables

A 3-stage framework for achieving sustainability

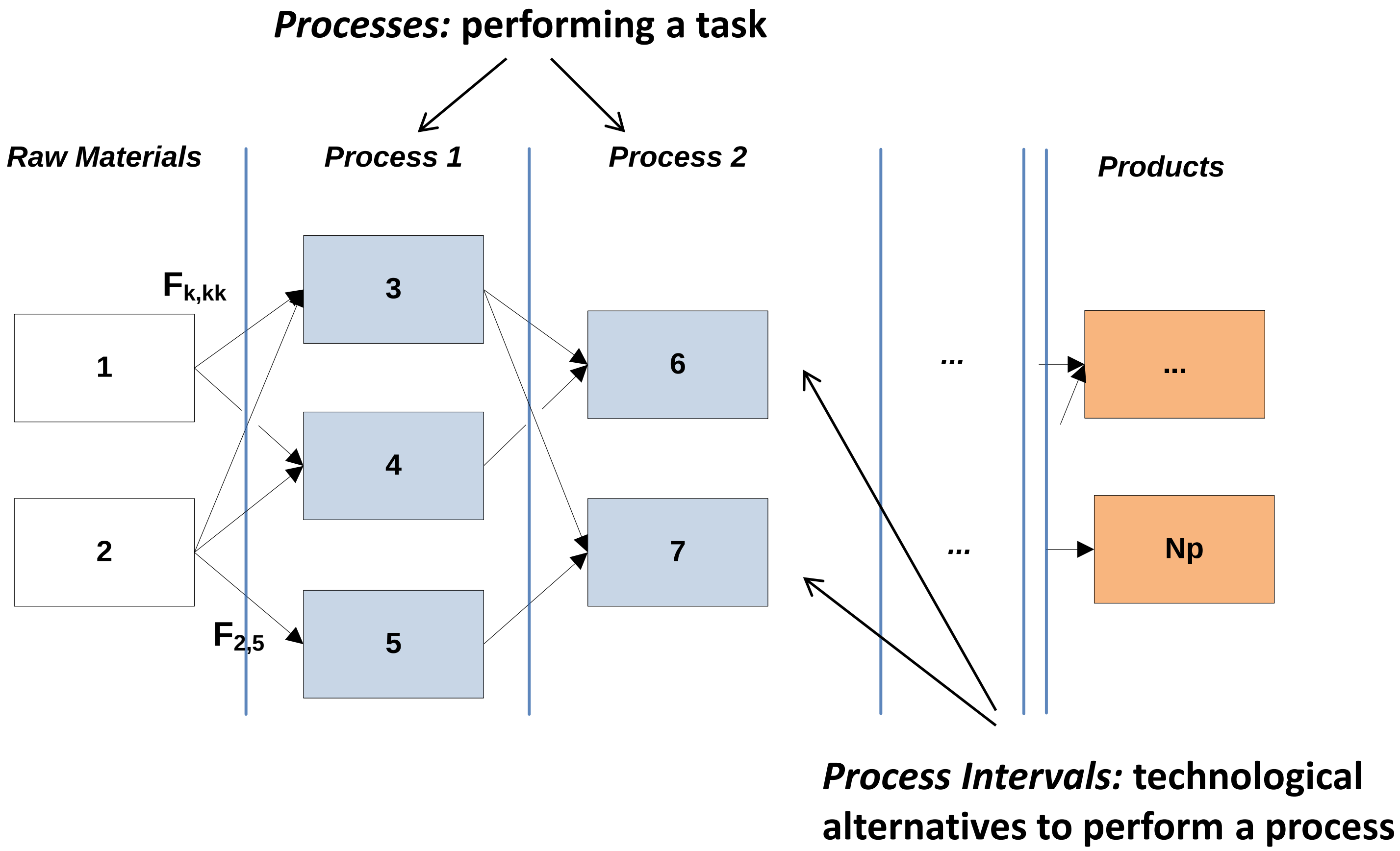


Different ways to find a processing route:

- **Existing processes**
- **Heuristic**
- **Mathematical programming**
- **Hybrid**

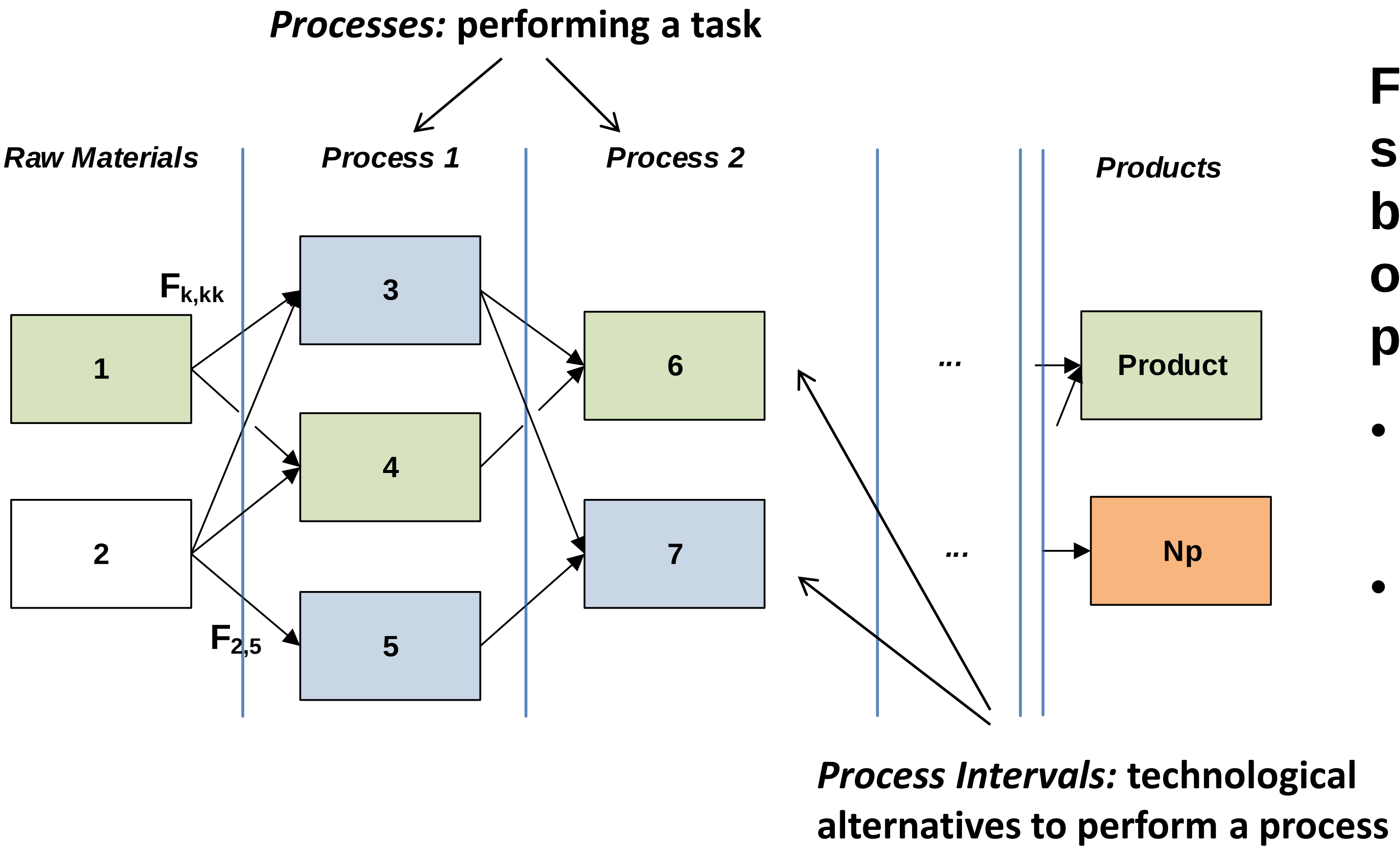
How to represent processing networks?

Superstructure of alternatives



How to find the optimal processing networks?

Model-based superstructure optimization



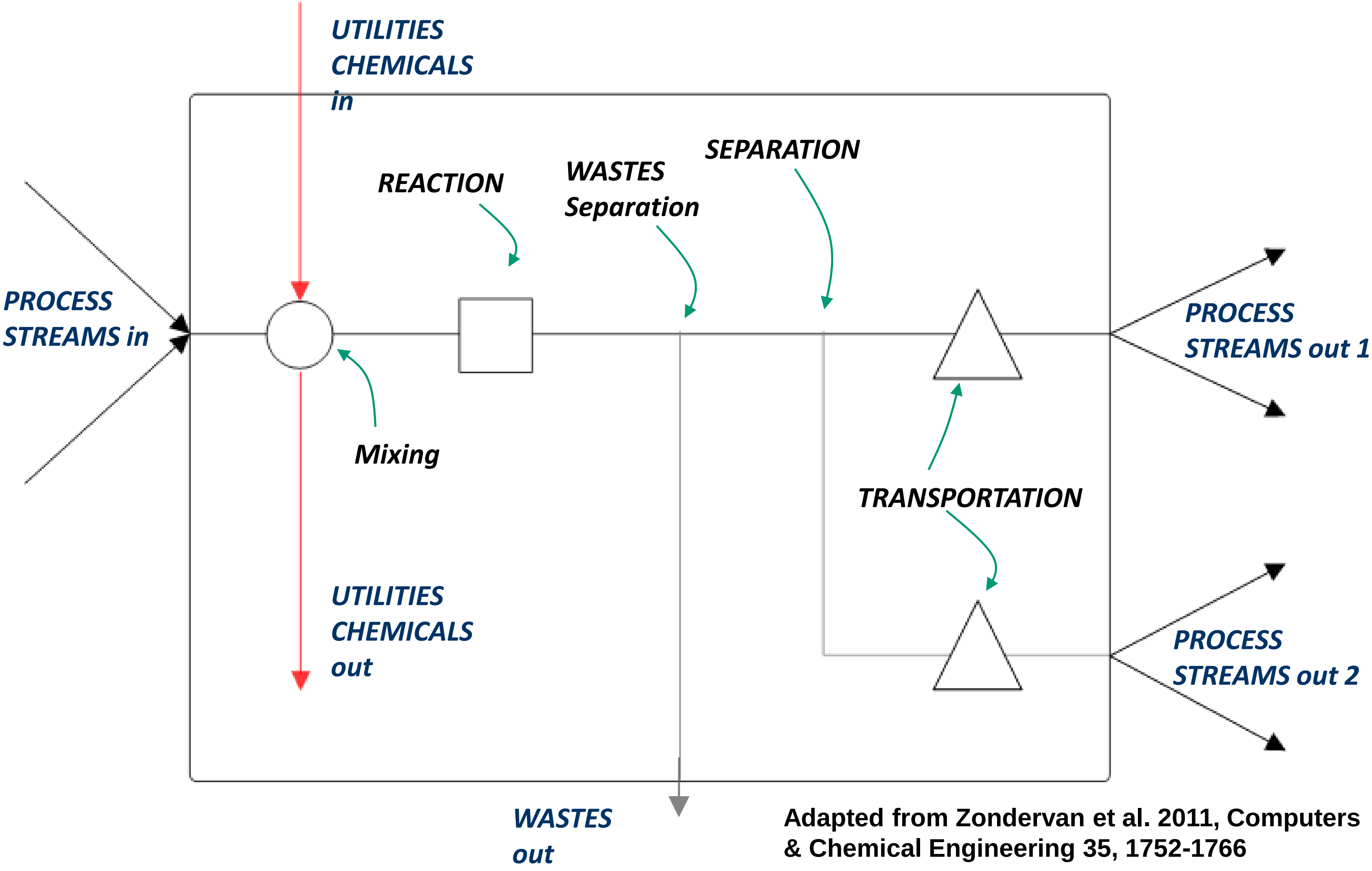
Processes: **performing a task**

Process Intervals: **technological alternatives to perform a process**

Formulate and solve a model-based optimization problem

- **Derive the model**
- **Solve the problem**

The generic process interval model



Adapted from Zondervan et al. 2011, Computers & Chemical Engineering 35, 1752-1766

Generic Model Equations and Data

MIXING	$F^{M}_{i,kk} = \sum_{k} \left(F_{i,k,kk} \right) + \alpha_{i,kk} \cdot R_{i,kk}$ $R_{i,kk} = \mu_{i,kk} \cdot \sum_{i,k} \left(F_{i,k,kk} \right)$
REACTION	$F^{R}_{i,kk} = F^{M}_{i,kk} + \sum_{rr,react} \left(\gamma_{i,kk,rr} \cdot \theta_{react,kk,rr} \cdot F^{M}_{reac,kk} \right)$
WASTES SEPARATION	$F^{out}_{i,kk} = F^{R}_{i,kk} \cdot \left(1 - SW_{i,kk} \right)$
PRODUCT SEPARATION	$F_{i,kk,kk} = F^{out}_{i,k} \cdot S_{k,kk} \cdot \varepsilon_{i,k,kk}$
TRANSPORTATION	$Ctr_{k,kk} = \sum_{i} F_{i,k,kk} \cdot W_{k,\ kk} \cdot dist_{k,kk}$
CAPEX	$CAPEX_{kk} = P_{kk} \cdot \sum \left(F^{out}_{i,kk} \right)^{Q_{kk}}$
OBJECTIVE FUNCTION	$EBIT = \sum_{i,k} \left(P^{prod}_{k} F^{OUT}_{i,k} - P^{raw}_{k} F^{OUT}_{i,k} - P^{util}_{k} R_{i,kk} - P^{waste}_{i,k} Waste_{i,kk} - \frac{CAPEX_{k}}{t} \right)$

🟩 data

Data:	**Source:**
Alternatives	Company (all)
Process related	Engineering
Prices and Market related	Marketing, procurement
Product related	Product engineering
Regulations related	Regulatory

Large number of equations and data

Multiple data type and sources

⬇

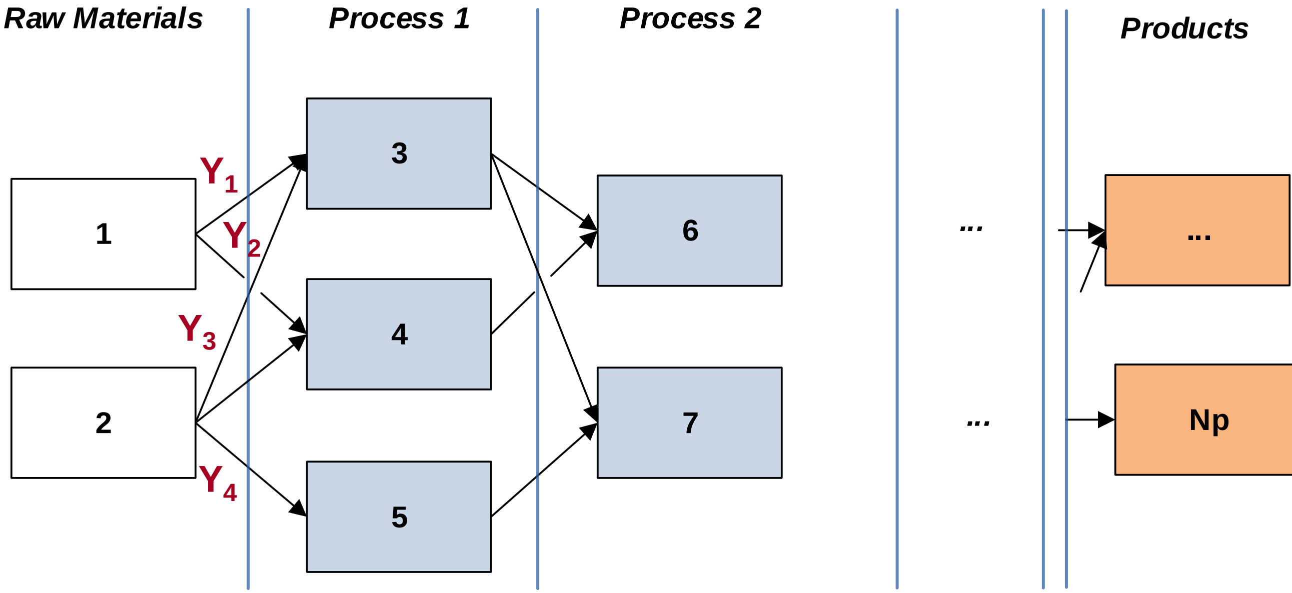
Need for Automation of problem formulation

General mathematical problem

$$F_{obj} = \min \{C^T\underline{y} + f(\underline{x}, \underline{y}, \underline{u}, \underline{d}, \underline{\theta}) + S_e + S_i + S_s + H_c + H_p\}$$

Process-product model

$$P = P(\underline{f}, \underline{x}, \underline{y}, \underline{d}, \underline{u}, \underline{\theta})$$



Process-product

$$0 = h_1(\underline{x}, \underline{y})$$

Equipment-material

$$0 \geq g_1(\underline{x}, \underline{u}, \underline{d})$$

$$0 \geq g_2(\underline{x}, \underline{y})$$

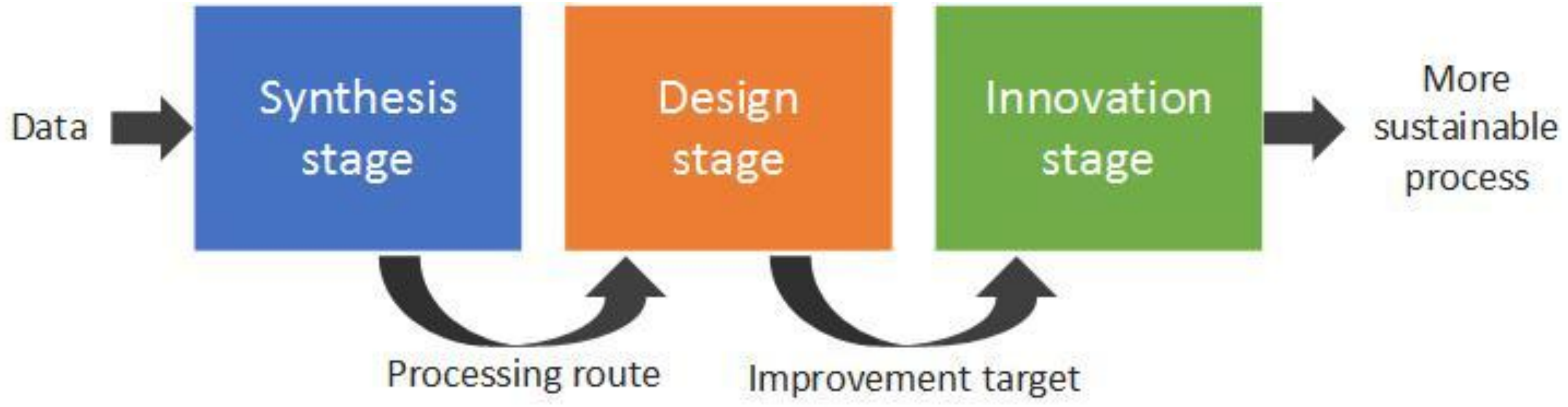
Flowhseet-chemical alternatives

$$B\,\underline{x} + C^T\underline{y} \geq D$$

$$\Sigma Y_i = 1 \text{ or } 1 \geq \Sigma Y_i \leq 2$$

Or, Set $Y_2 = 0$

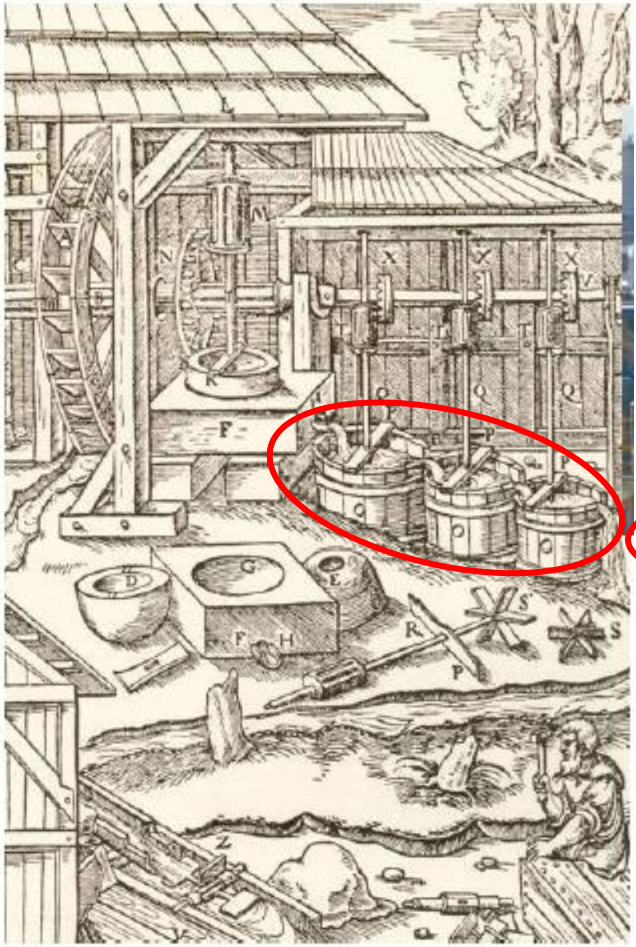
A 3-stages framework for achieving sustainability



Innovation stage: Tailor-made process design

- Generate alternatives that match specified design targets
- Order solutions that give the best

Why we need innovative solutions?



G. Agricola, *De Re Metallica*, 1556

Innovations – Unit operations

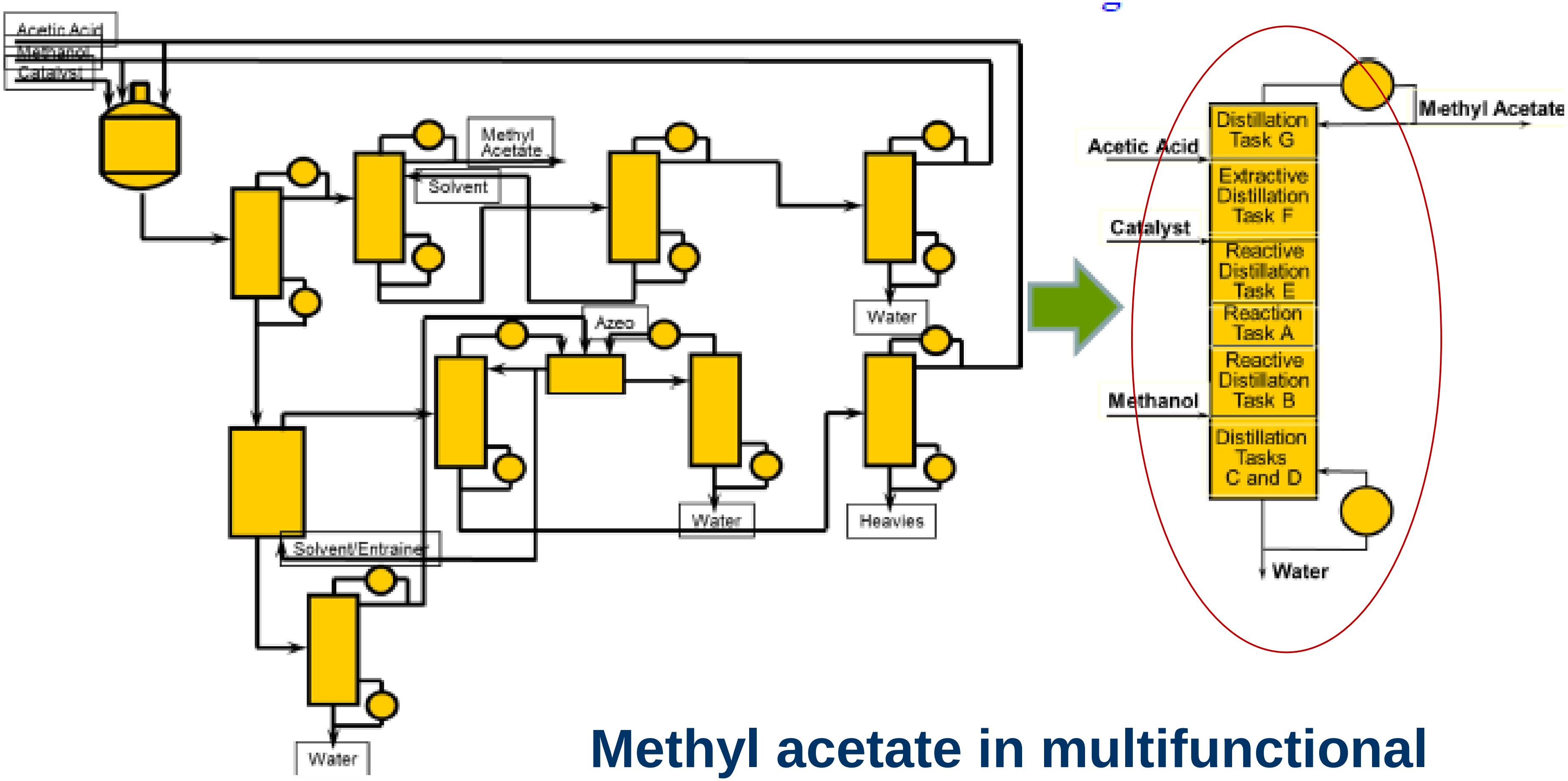
Chemical Process Industry, 2006

Is it possible to achieve more improvements in design for this equipment (unit operation)?

Adapted from Stankiewicz, 2008

Why we need innovative solutions?

Example of process intensification



Methyl acetate in multifunctional reactor (Eastman Chemicals)

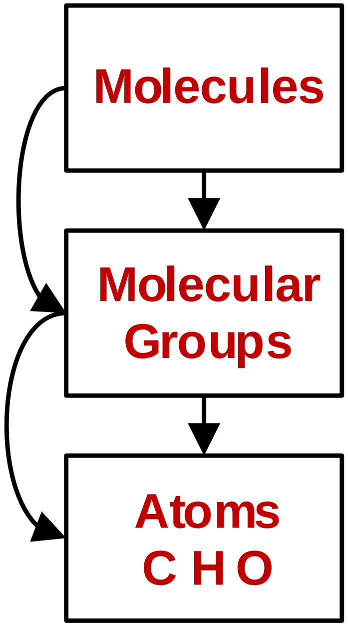
Concept: Generation of alternatives

Molecular design vs flowsheet design

- Comparison to Computer-Aided Molecular Design (CAMD)
- **Key concept**: Operation at a lower level of aggregation

Lower Level of Aggregation

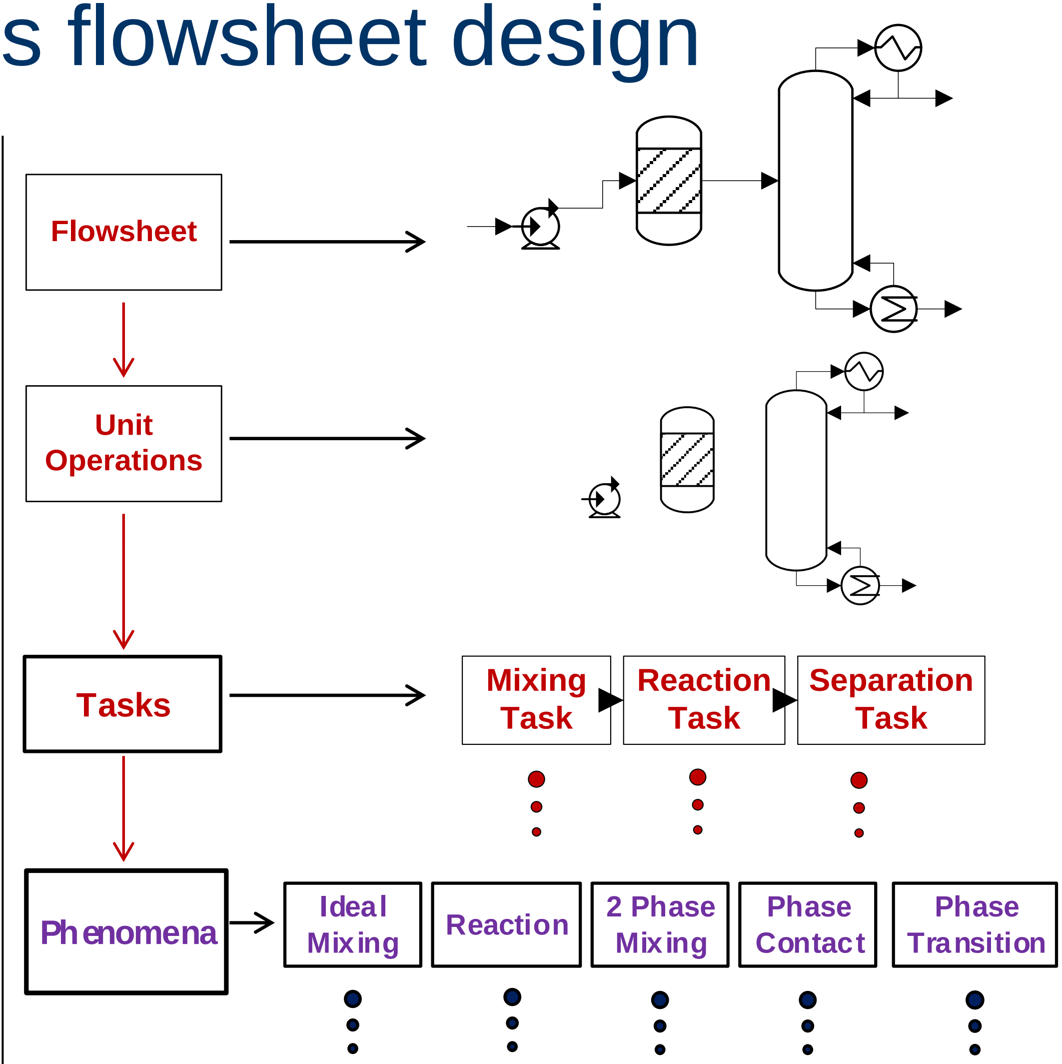
Next Lower Level of Aggregation


Molecules

Molecular Groups

Atoms
C H O

Gani et al. (1994)


Flowsheet

Unit Operations

Tasks

Mixing Task

Reaction Task

Separation Task

Phenomena

Ideal Mixing

Reaction

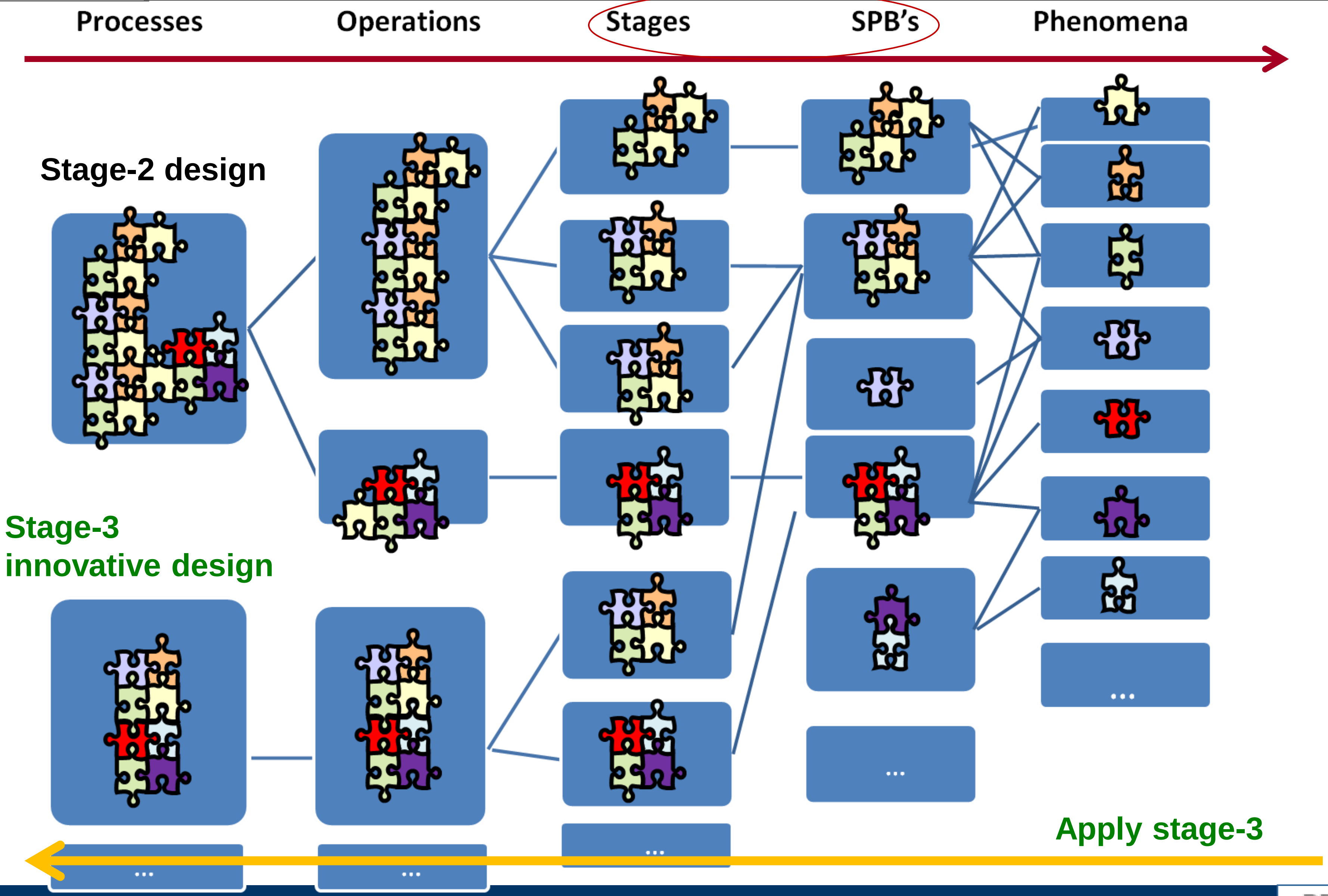
2 Phase Mixing

Phase Contact

Phase Transition

Babi et al. (2014)

Flowsheet to phenomena: Both ways



Processes | Operations | Stages | SPB's | Phenomena

Stage-2 design

Stage-3 innovative design

Apply stage-3

Tasks to Phenomena (SPB)

R, M_I, M_T, M_R M_V, 2phM, PC(V-L), PT(V-L), PT(P:V-L), PS (V-L), D, H, C
13 in total

SPB	Interconnection Phenomena	In	Out
SPB.1	M	1..n(L)	1(L)
SPB2	M=R	1..n(L)	1(L)
SPB.7	M=R=2phM=PC=PT(VL)	1..n(L,VL)	1(V/L)
SPB.8	M=R=2phM=PC=PT(VL)=PS(VL)	1..n(L,VL)	2(V;L)
SPB.9	M=R=2phM=PC=PT(PVL)=PS(VL)	1..n(L,VL)	2(V;L)
SPB.58	D	1(L;VL,V)	1..n(L;V; VL)

Reduced from 4017→58 using connectivity rules

<u>Connectivity Rules:</u>

1. **H+C should not exist in the same SPB**
2. **PC phenomena exists together with PT phenomena**
3. **SPB can contain simultaneous R and separation**

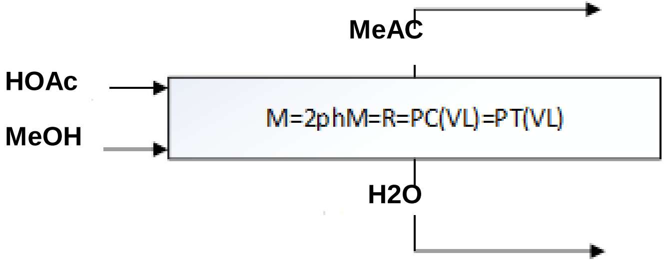
SPB	Interconnection Phenomena	In	Out
	~~M=R=H=C~~	~~1..n(L)~~	~~1(L)~~

SPB	Interconnection Phenomena	In	Out
SPB.7	M=R=2phM=PC=PT(VL)	1..n(L,VL)	1(V/L)

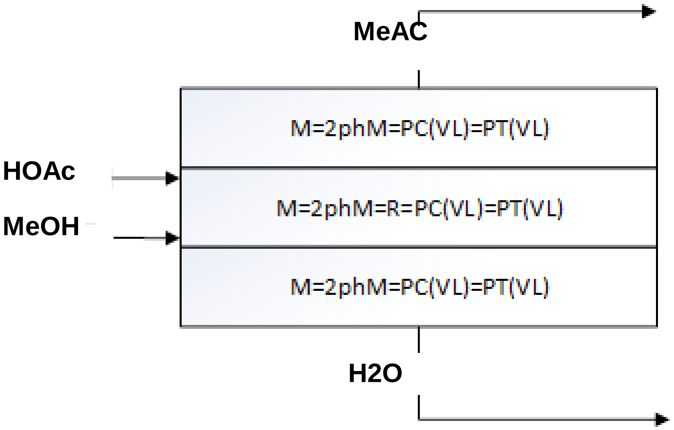
SPB	Interconnection Phenomena	In	Out
SPB.8	M=R=2phM=PC=PT(VL)=PS(VL)	1..n(L,VL)	2(V;L)
SPB.9	M=R=2phM=PC=PT(PVL)=PS(VL)	1..n(L,VL)	2(V;L)

Lutze et al. (2013)

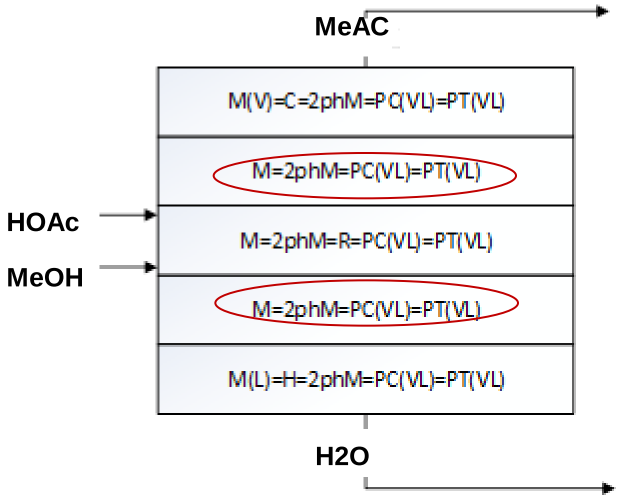
Combine phenomena: New operations



Not feasible*

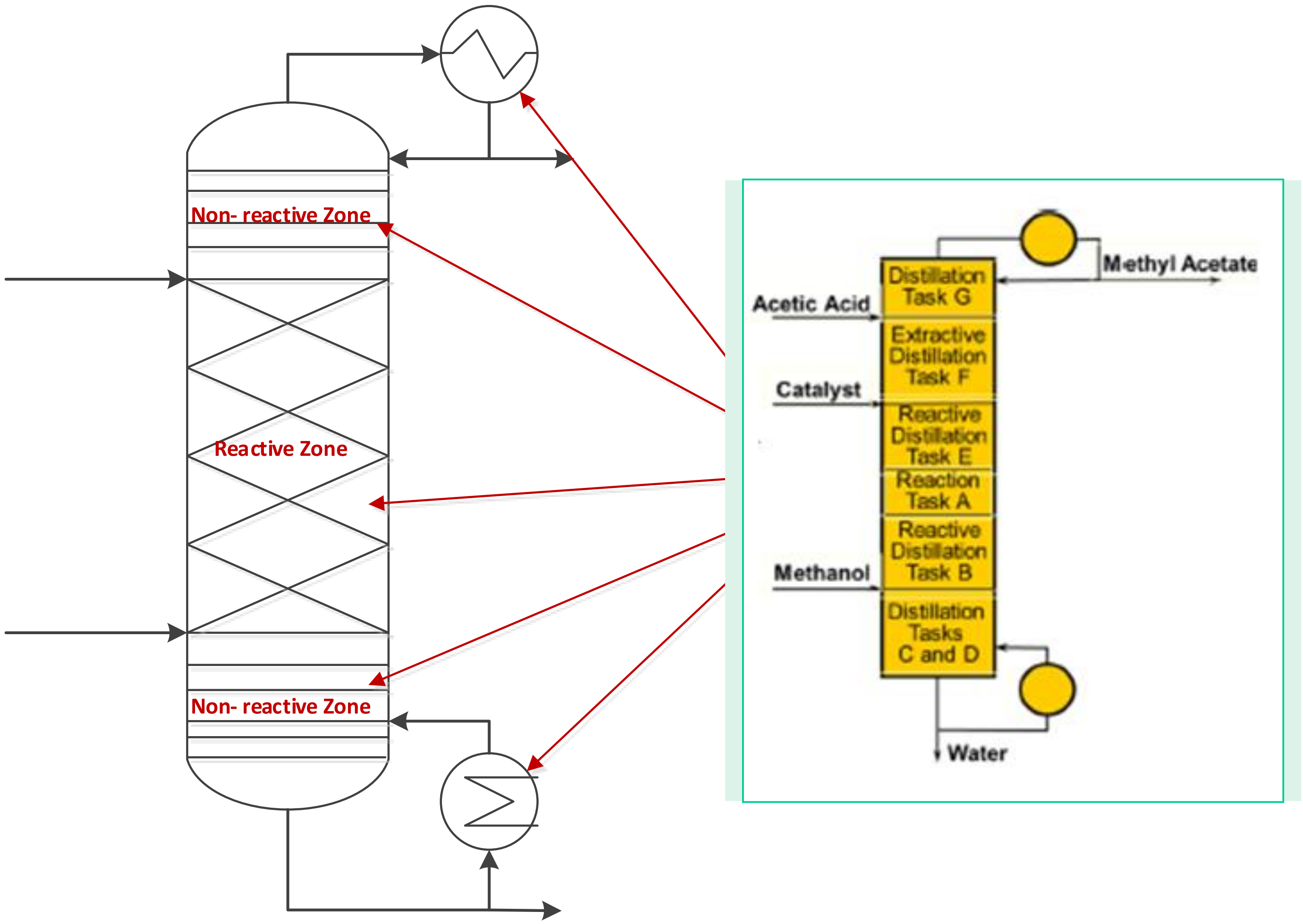


Feasible*



**** With respect to the target***

Innovative solution

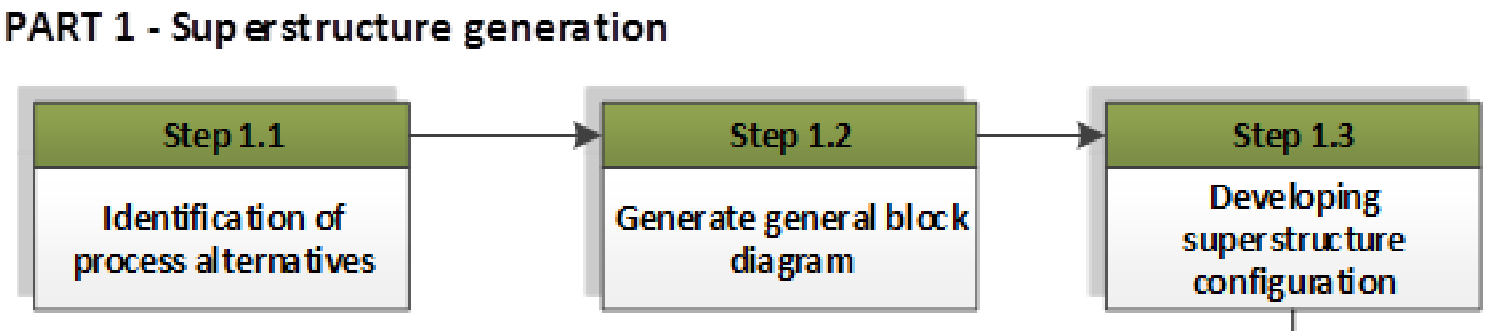


Examples: Energy, Water, Food Nexus

- **Biodiesel case study (stages 1-3)**
- **Edible oil enterprise network (stage-1)**
- **CO2 utlization networks (stages 1-2)**
- **Wastewater reuse network (stages 1-3)**
- **Biorefinery project (stages 1-3)**
- **……**

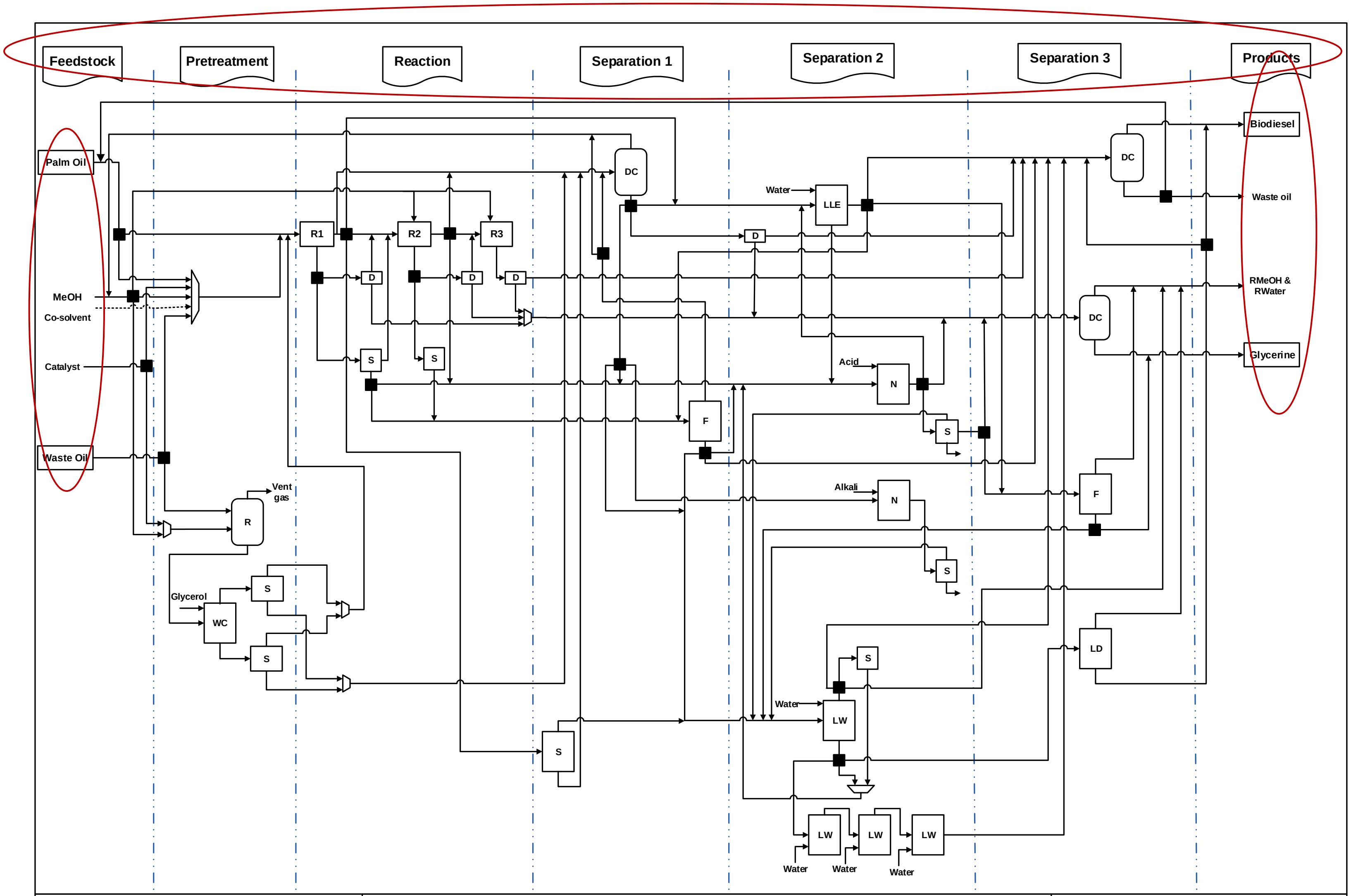
Example: Biodiesel production

- **Two raw material sources (palm oil & waste (cooking) palm oil) having different compositions**
- **Flowsheet depends on the conversion technique employed (11 different catalysts found)**
- **Same product specifications**



Mansouri et al. (2013)

Biodiesel production superstructure



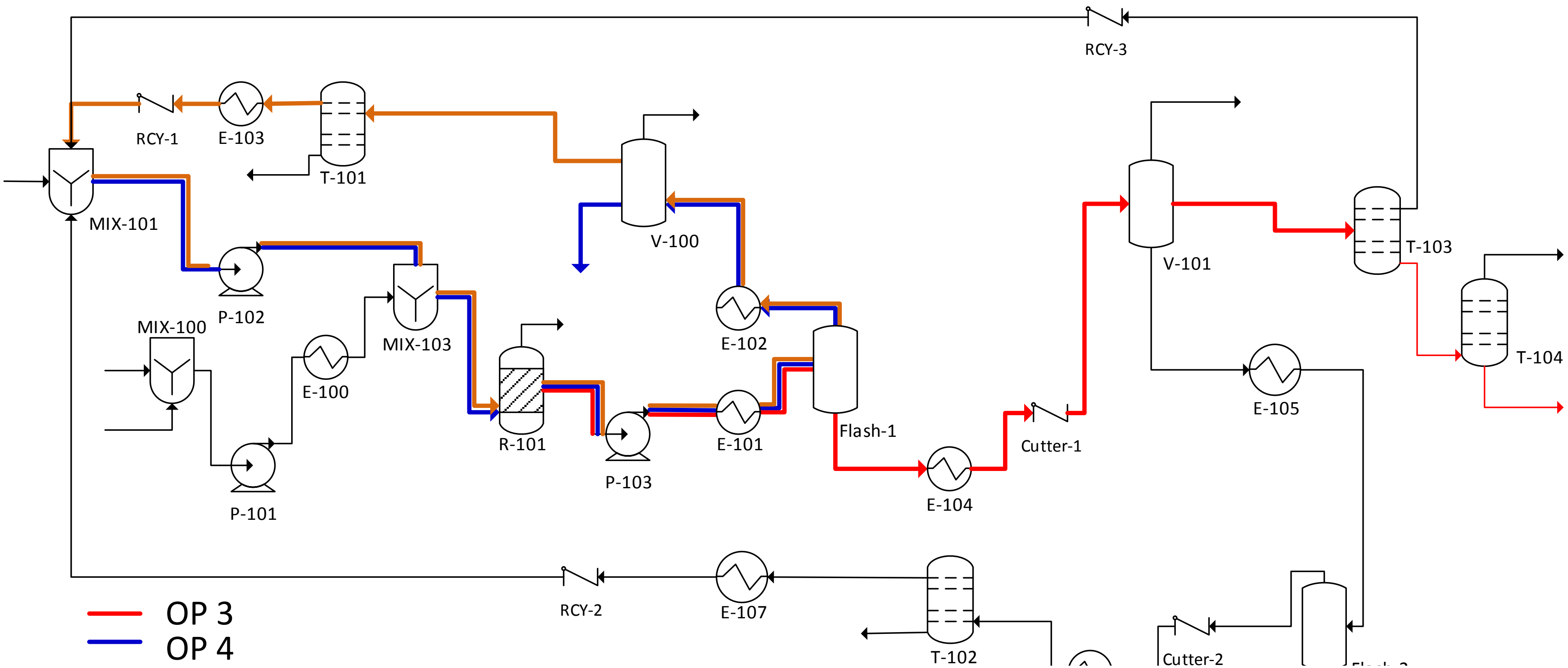
Title: Superstructure biodiesel production
Details: Combination of flowsheets

Legend:

R - Reactor
D - Decanter
S - Separator
WC - Washing column
E - Esterification Tank
LLE - Liquid-liquid extraction
DC - Distillation column
LD - Liquid dryer
LS - Liquid separator
F - Flash
N - Neutralization tank
LW - Liquid washing

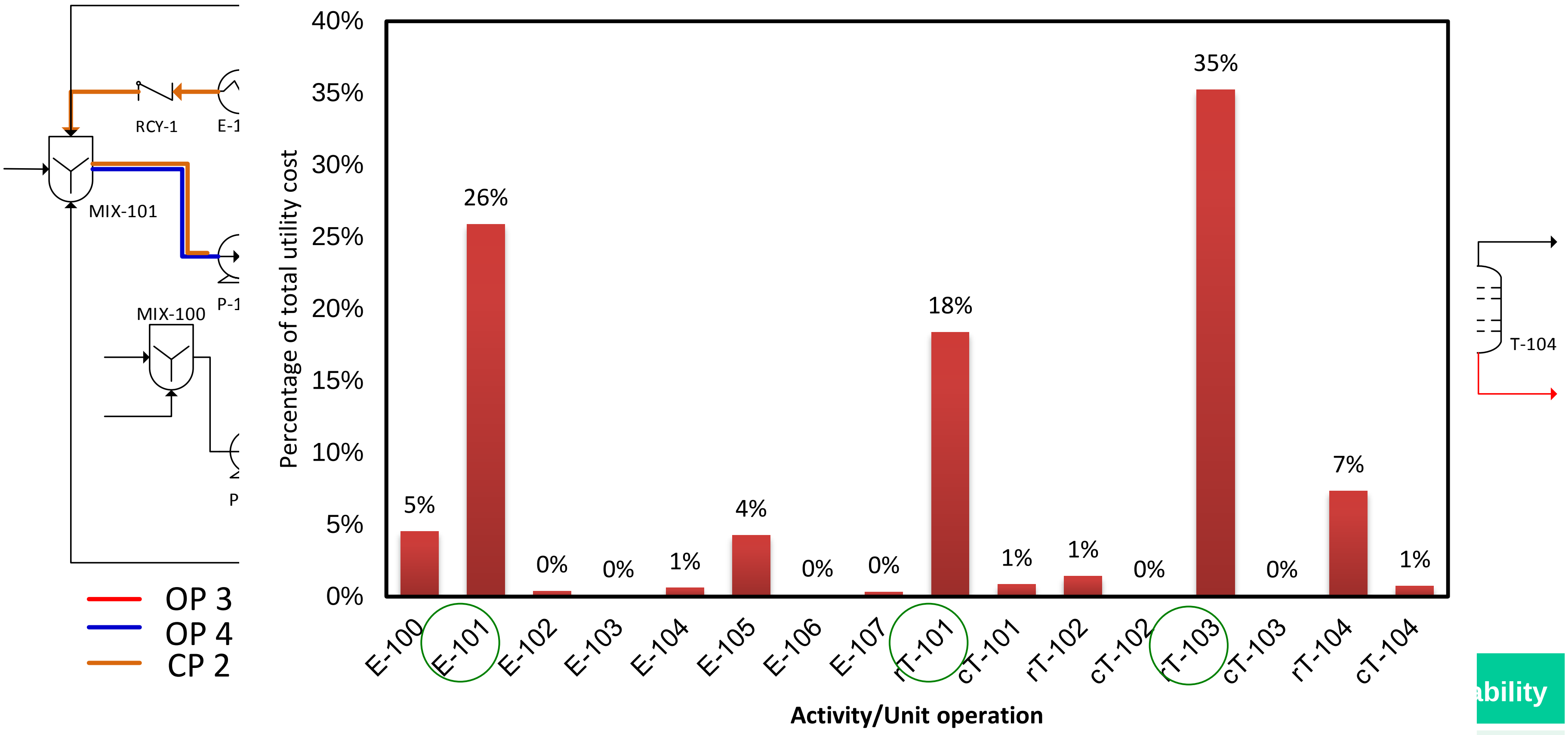
Sep 1 - Methanol recovery
Sep 2 - Water washing and neutralization
Sep 3 - Biodiesel and glycerine purification

Biodiesel production: Base case analysis



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: Base case analysis



					ability
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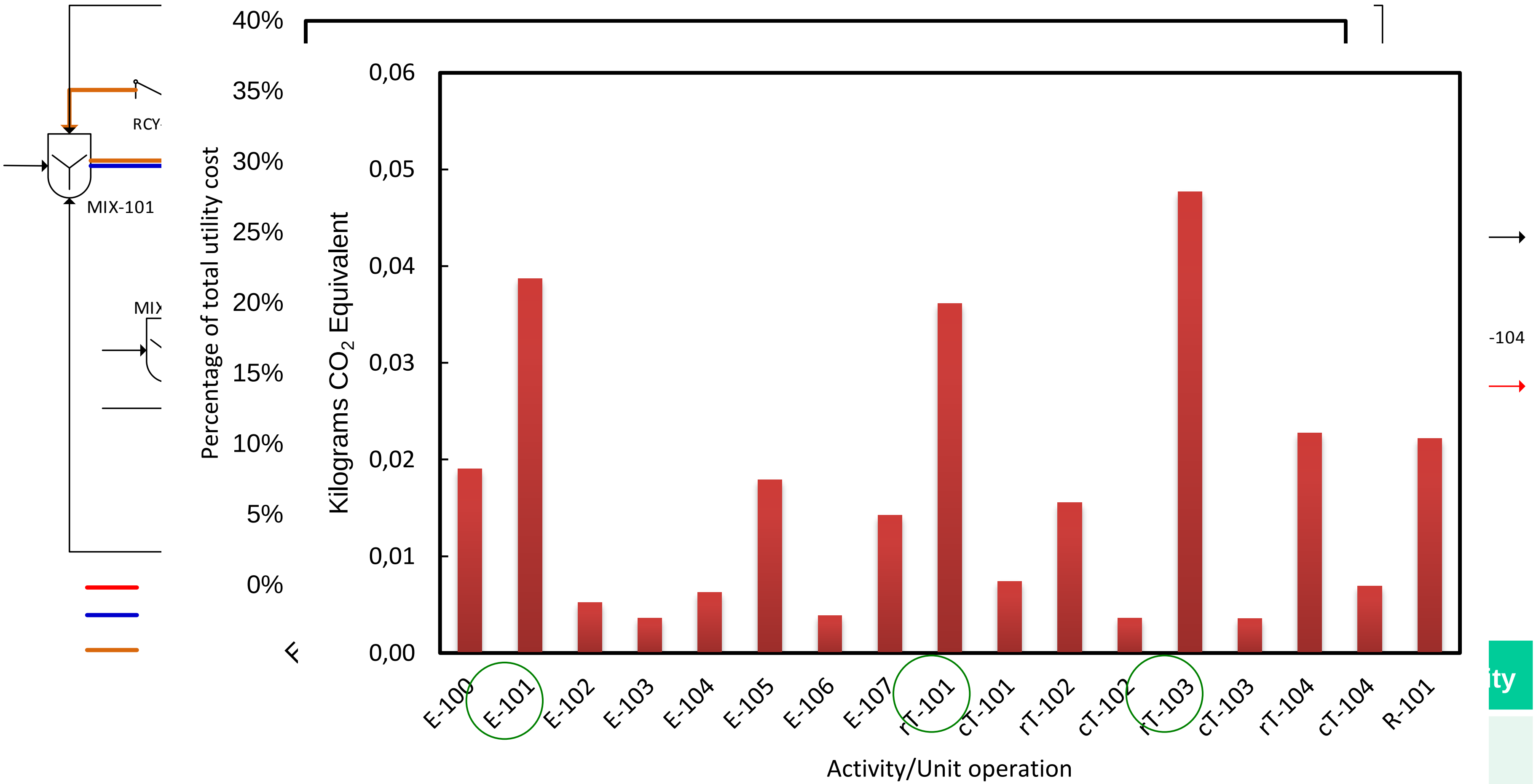
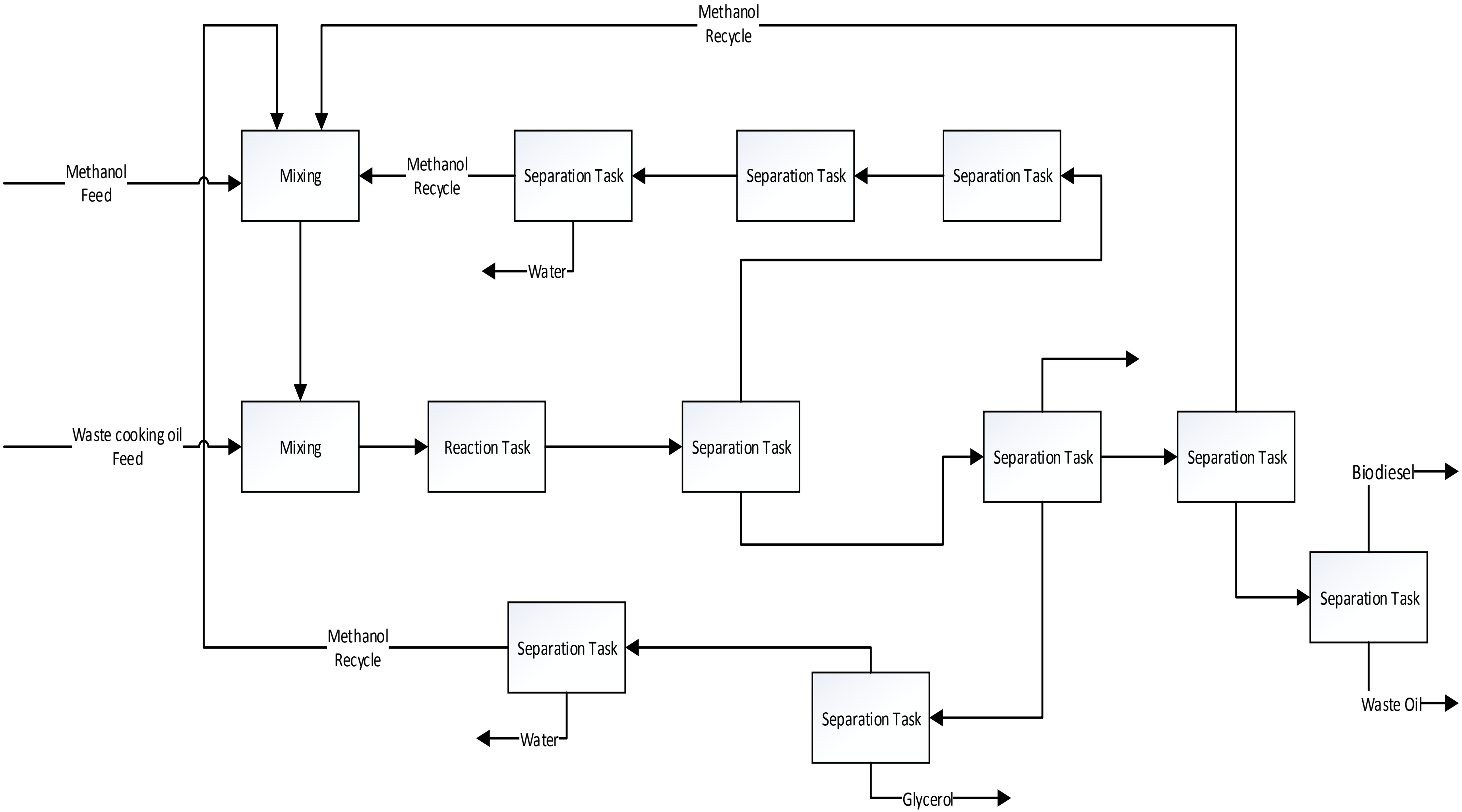
Biodiesel production: Base case analysis

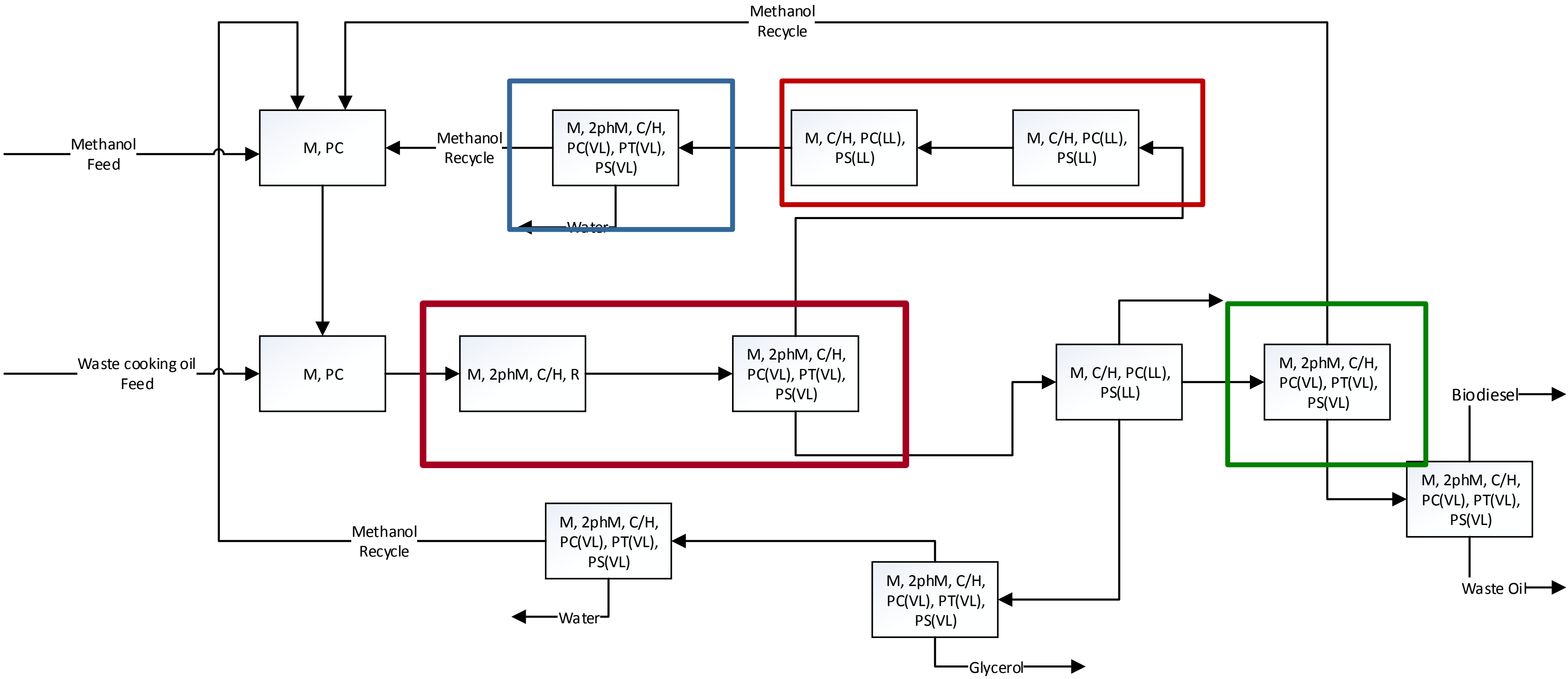


OP4	–2047.234859	High	-	-	-
C 2	496.6545095	High	C2	496.6545095	High

Biodiesel production: Identify tasks

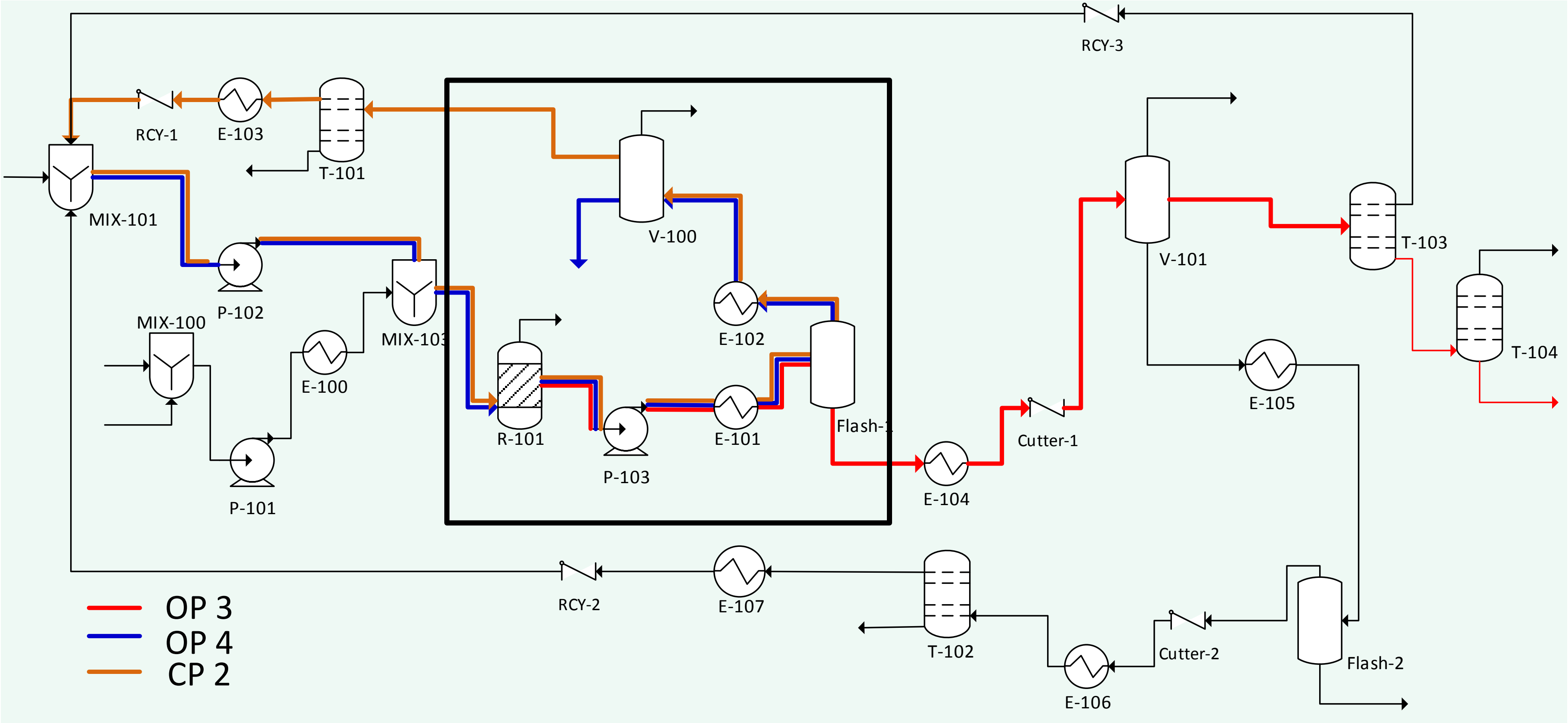


Base case analysis: Identify phenomena



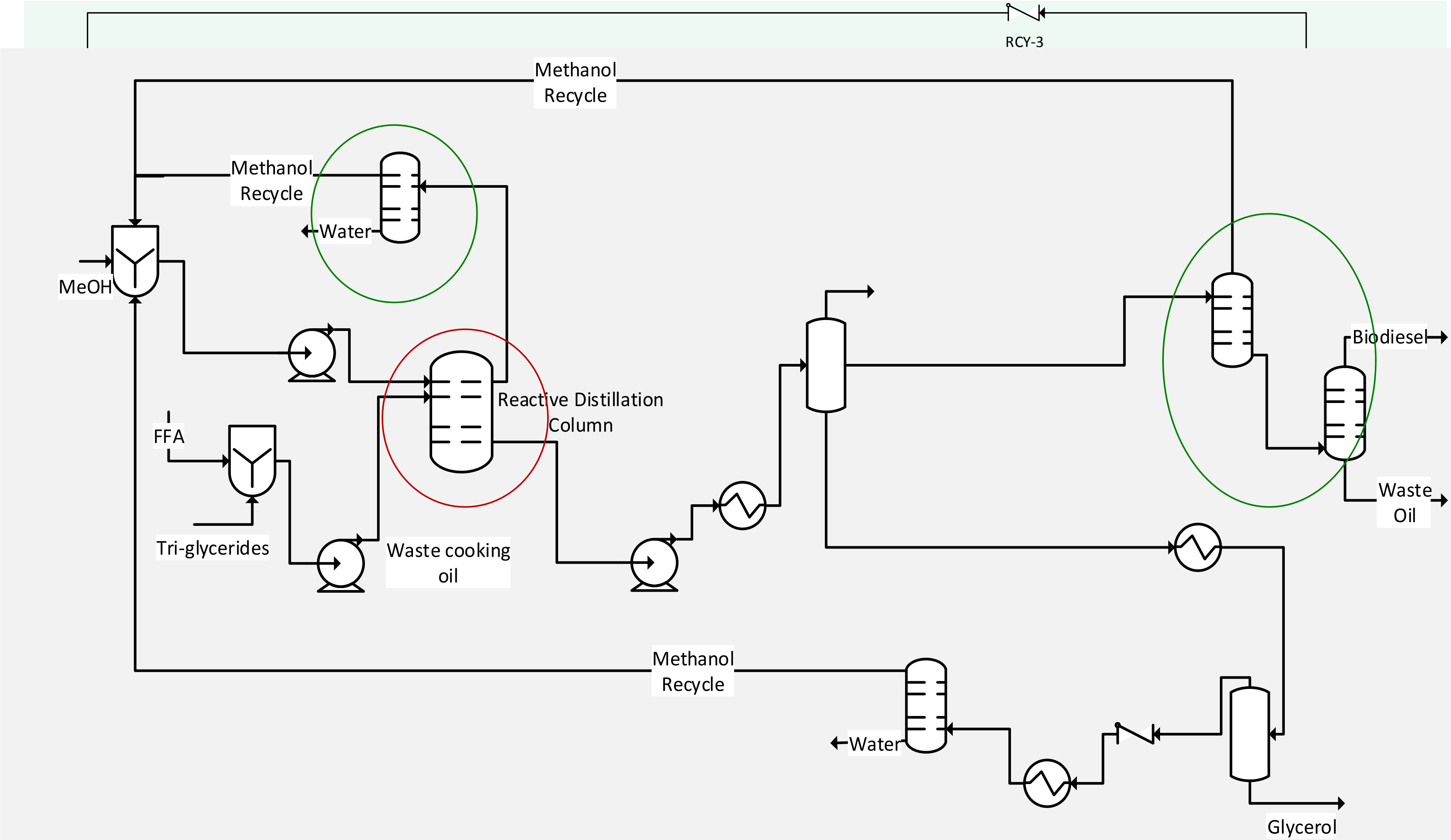
Mansouri et al. 2013

New more sustainable (PI) solution



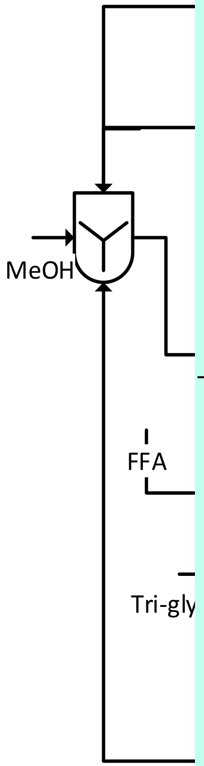
Mansouri et al. 2013

New more sustainable (PI) solution



Mansouri et al. 2013

New more sustainable (PI) solution



	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

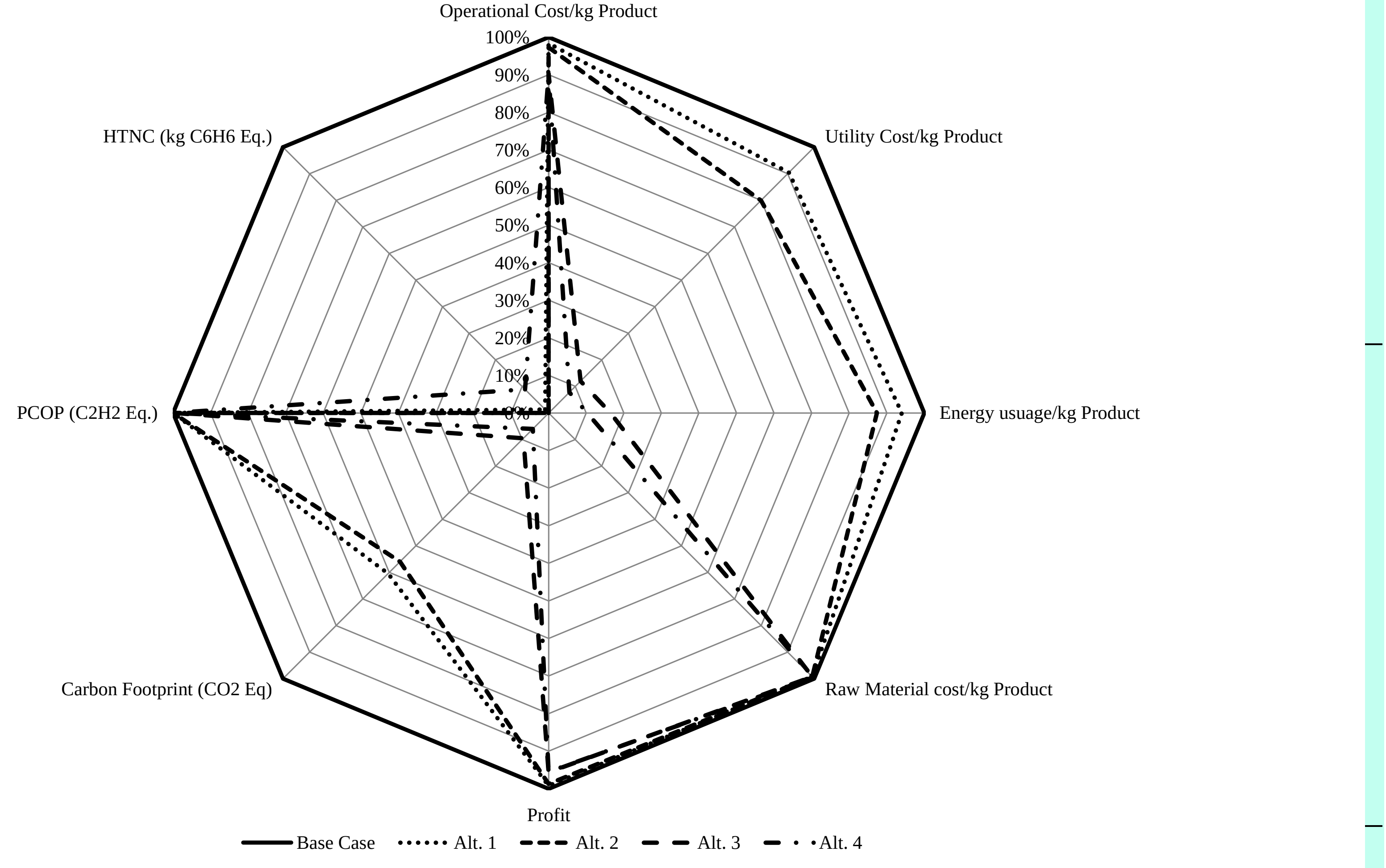
LC_{50} is lethal concentration ($mg_{emission}/kg_{fathead\ minnow}$)

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

Mansouri e

New more sustainable (PI) solution

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 e

Edible oil industry: Soybean Processing

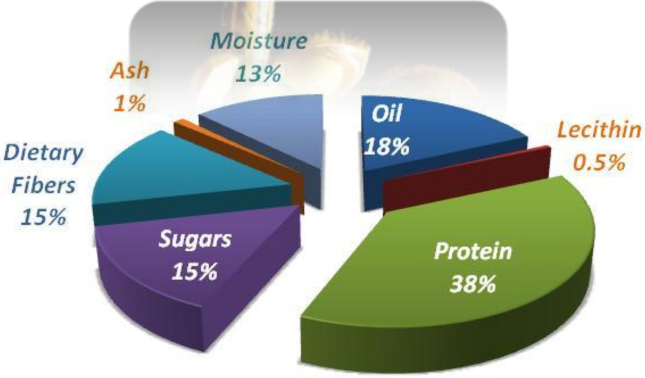
Soybean *(Glicine max)*:
native to East Asia, globally grown.
248 MMT global production*, steadily increasing

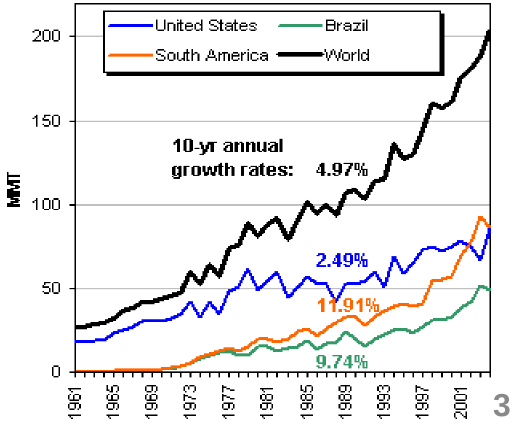
Goal:
Synthesis and Design of Optimal Soybean Processing Network
Maximize Net Present Value (**NPV**)
Robustness to Uncertainty

Models:
Generic Process Interval Model

Sources of uncertainty:
Commodity - price uncertainty
Natural product - raw material composition uncertainty

Raw Materials	*2*
Products	*21*
Processes	*15*
Proc. Intervals	*42*
Tot binary var.	*65*





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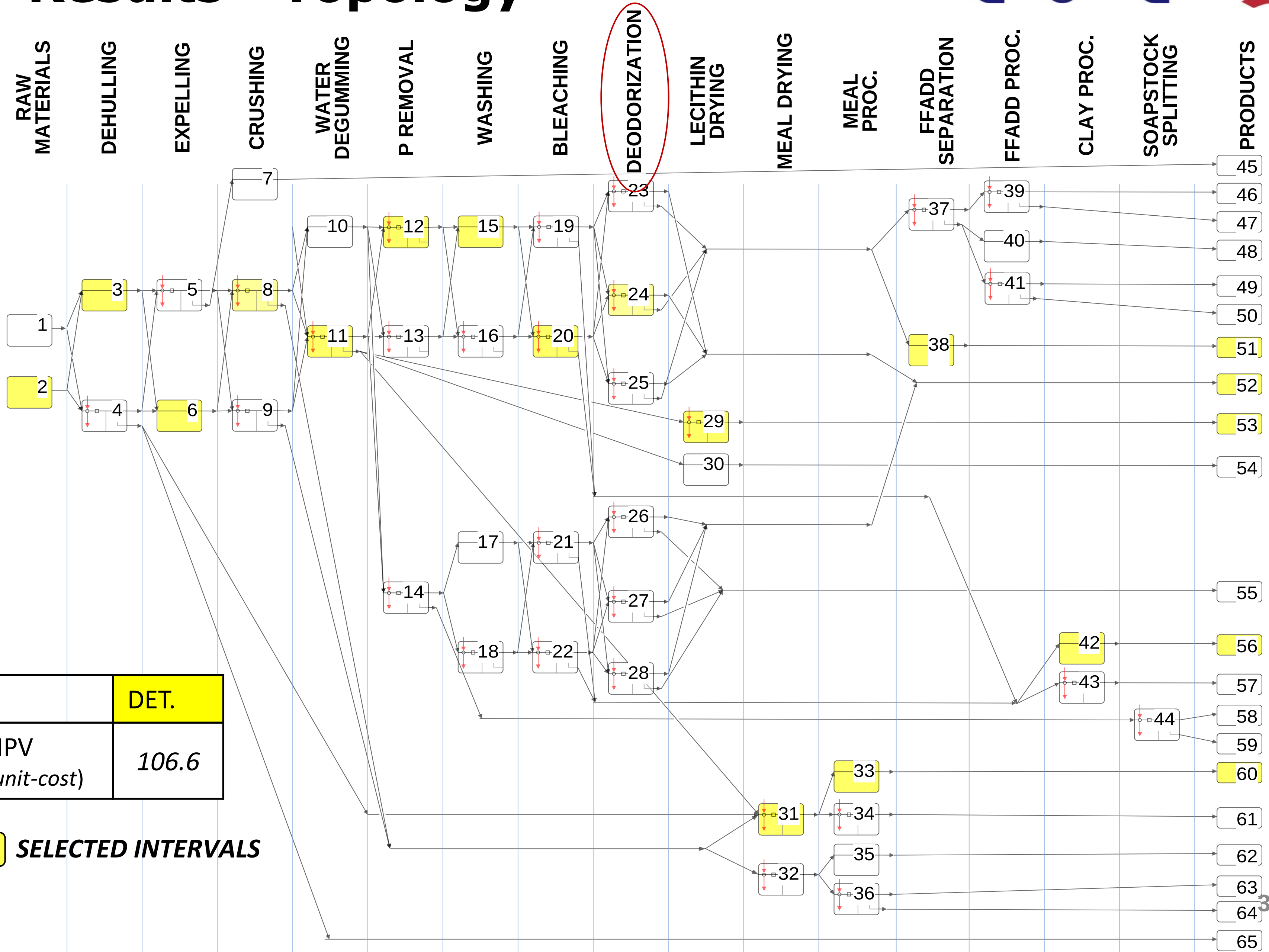
* *FAO Food Outlook*, 2007-2009

Results - Topology



RAW MATERIALS

DEHULLING

EXPELLING

CRUSHING

WATER DEGUMMING

P REMOVAL

WASHING

BLEACHING

DEODORIZATION

LECITHIN DRYING

MEAL DRYING

MEAL PROC.

FFADD SEPARATION

FFADD PROC.

CLAY PROC.

SOAPSTOCK SPLITTING

PRODUCTS

	DET.
NPV *(unit-cost)*	*106.6*

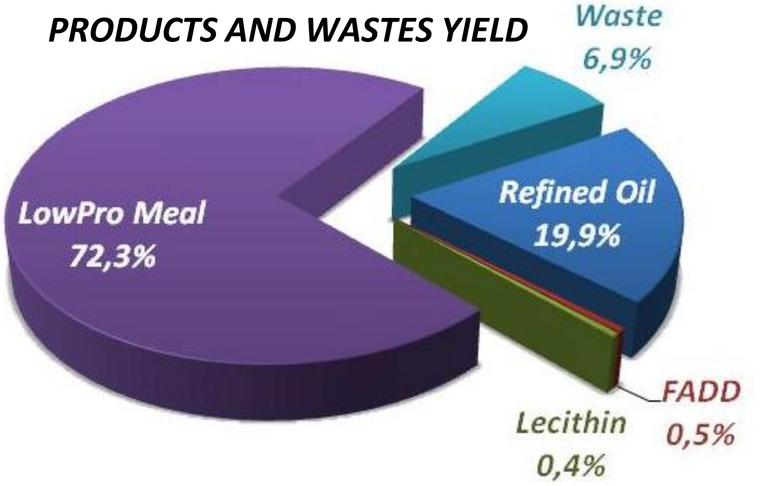
🟨 ***SELECTED INTERVALS***

Results 2 – Economics

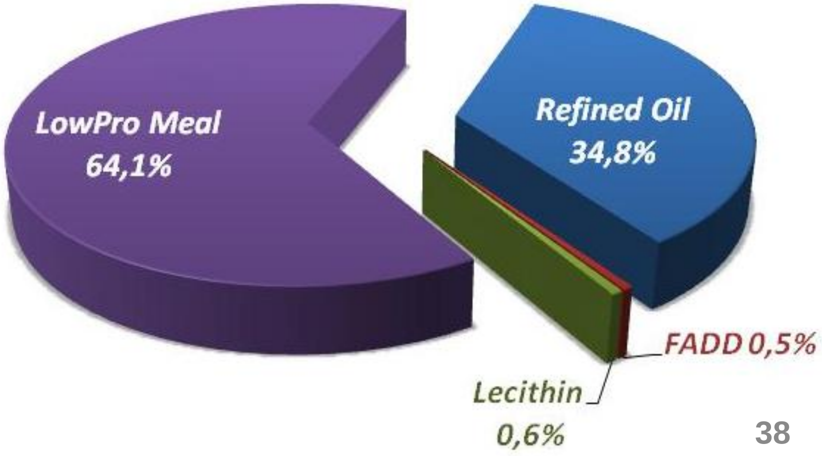
COST STRUCTURE OVERVIEW*

Cost	***unitcost***	**364.92**
Raw Material cost	*unitcost*	350.00
Utility cost	*unitcost*	11.88
(of which heat)	*unitcost*	(8.65)
Transportation	*unitcost*	-
Special Wastes Cost	*unitcost*	3.04
Revenues	***unitcost***	**492.61**
Oil	*unitcost*	158,26
Byproducts	*unitcost*	334.35
Gross Operating Margin	***unitcost***	**127.69**
Input to Product ratio	*%mass*	93.09%
Input to Wastes ratio	*%mass*	6.91%

PRODUCTS AND WASTES YIELD



REVENUES BREAKDOWN



**in scaled units, numbers refered to 100 unitmass of feed*

Oil Refinery Wastewater Treatment

- World refinery capacity: $88.7\cdot10^6$ barrels of crude oil per day (2010)[1]
- Single refinery capacity:150-600,000 barrels of crude oil per day[2]

- Average **freshwater consumption**: **1.55-2.14 tons/m^3 of crude oil**[3] → up to $30\cdot10^6$ ton/day!
  Average **wastewater production**: **0.48-0.95 tons/m^3 of crude oil**[3]

- Challenging case study:
  - **Intensive use** of water
  - Often located in **water scarce countries**
  - **Different configurations** of water user and producer processes
  - **Highly variable** amount and contamination of wastewaters

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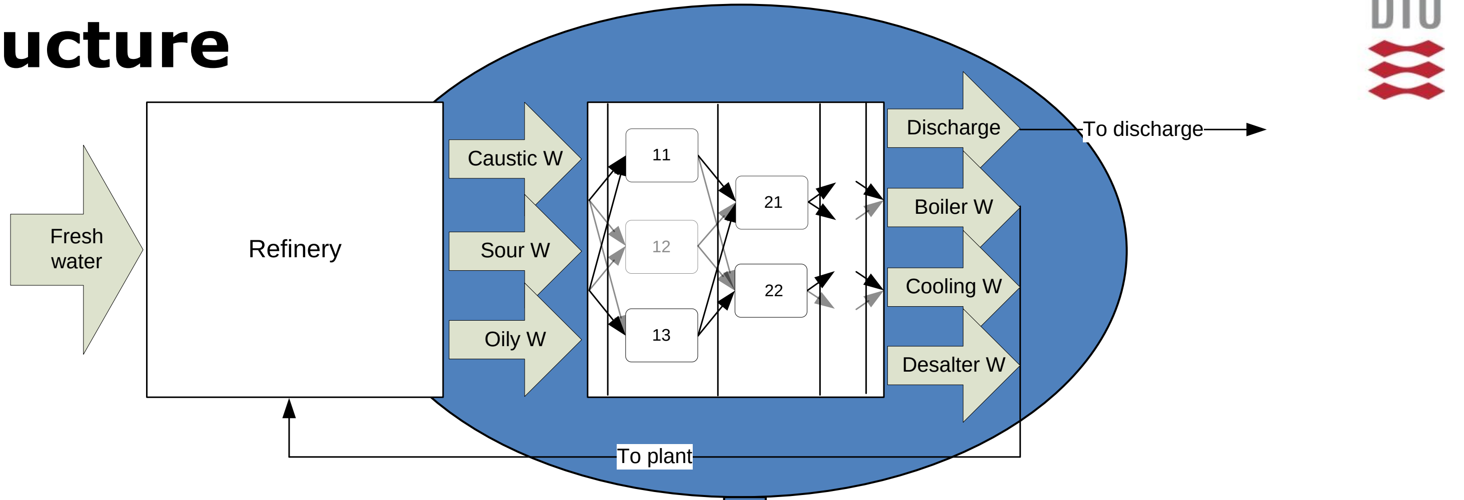
[1] OPEC, Annual Statistical Bulletin 2010/2011

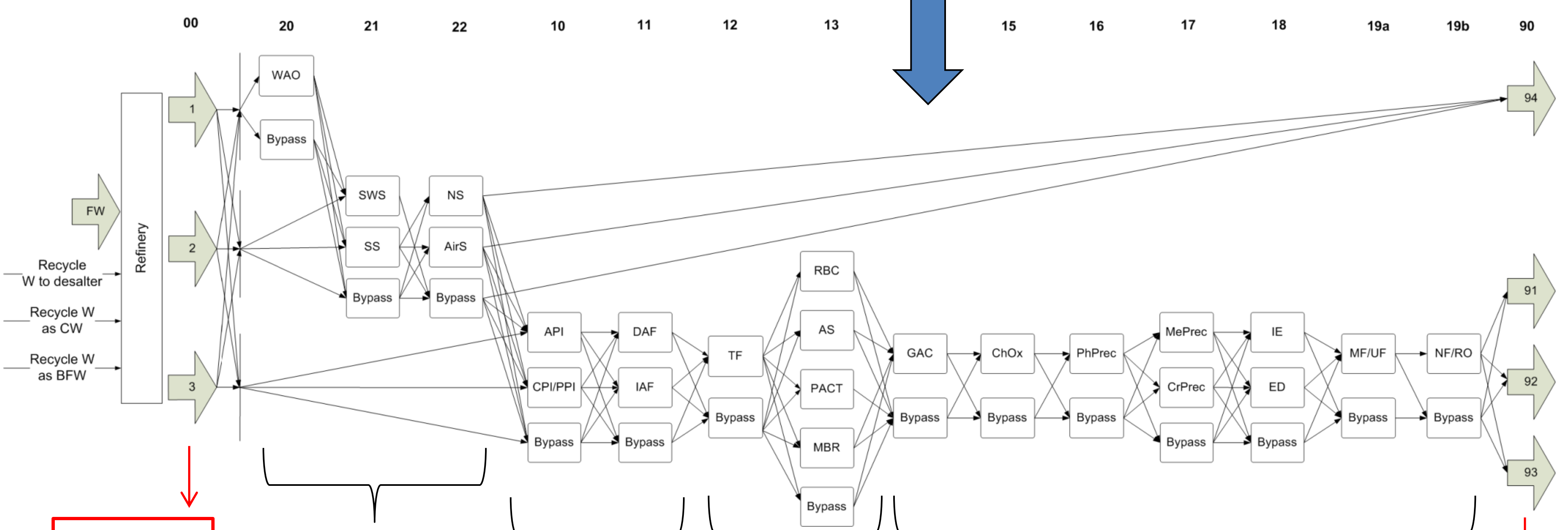
[2] J. Wong and Y. T. Hung, Handbook of Industrial and Hazardous Waste Treatment, 2004

[3] Adapted from DOE, Energy and Environmental Profile of of the U.S. Petroleum Refinery Industry, 2007

Superstructure

3 Wastewater Sources
4 Water Sinks
23 Treatment Units





Sources

Pre Treatment

H_2S, NH_4^+

Primary Treatment

SS, O&G, C

Secondary Treatment

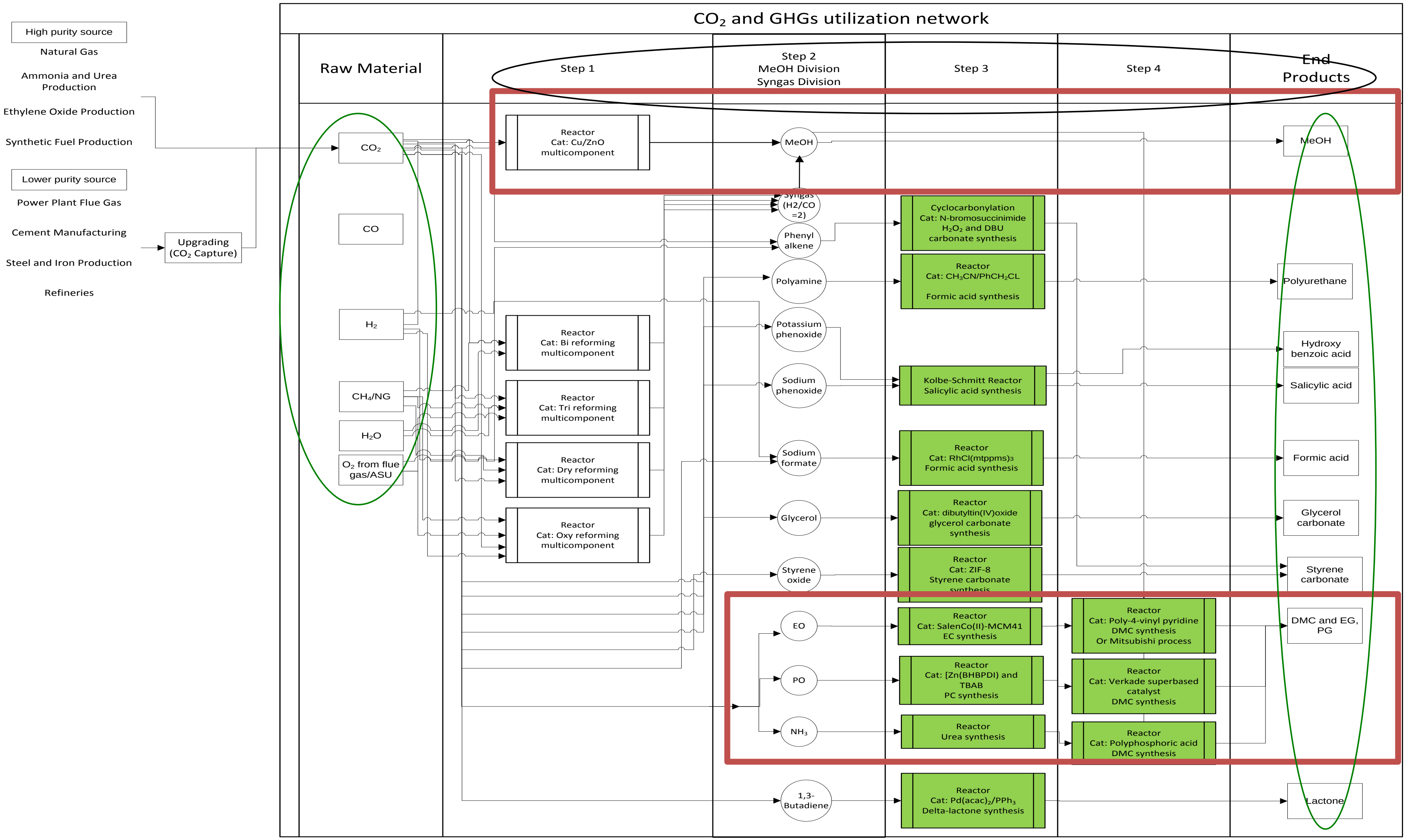
C

Tertiary Treatment

NH_4^+, Cr_6^+, ions

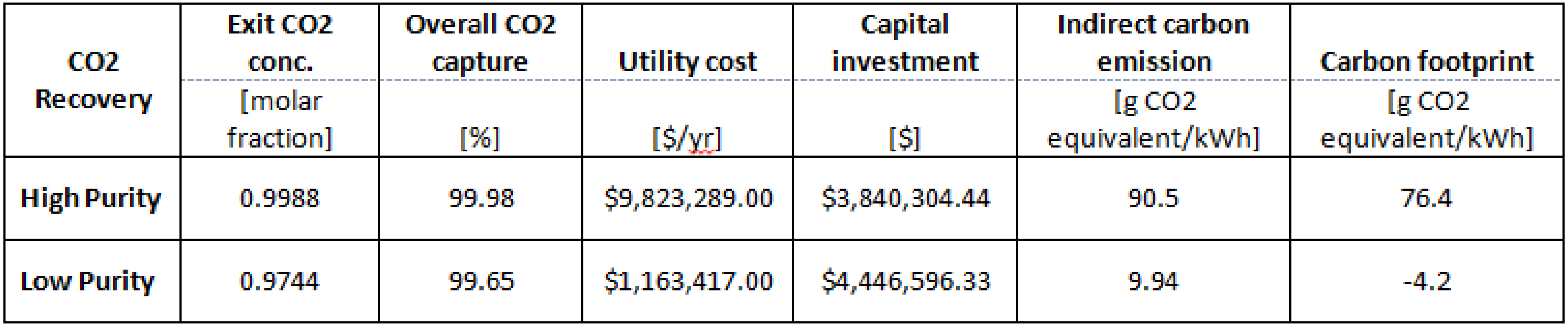
Sinks

CO2 Utilization



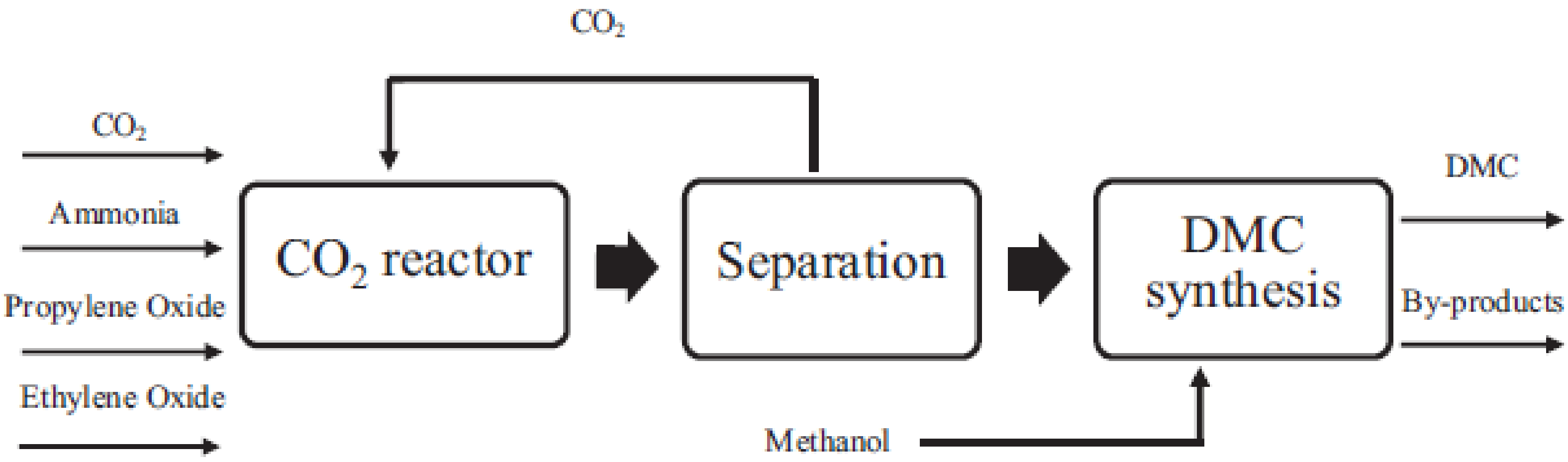
Production of chemicals through CO2 capture & conversion

Redesign of CO2 capture process



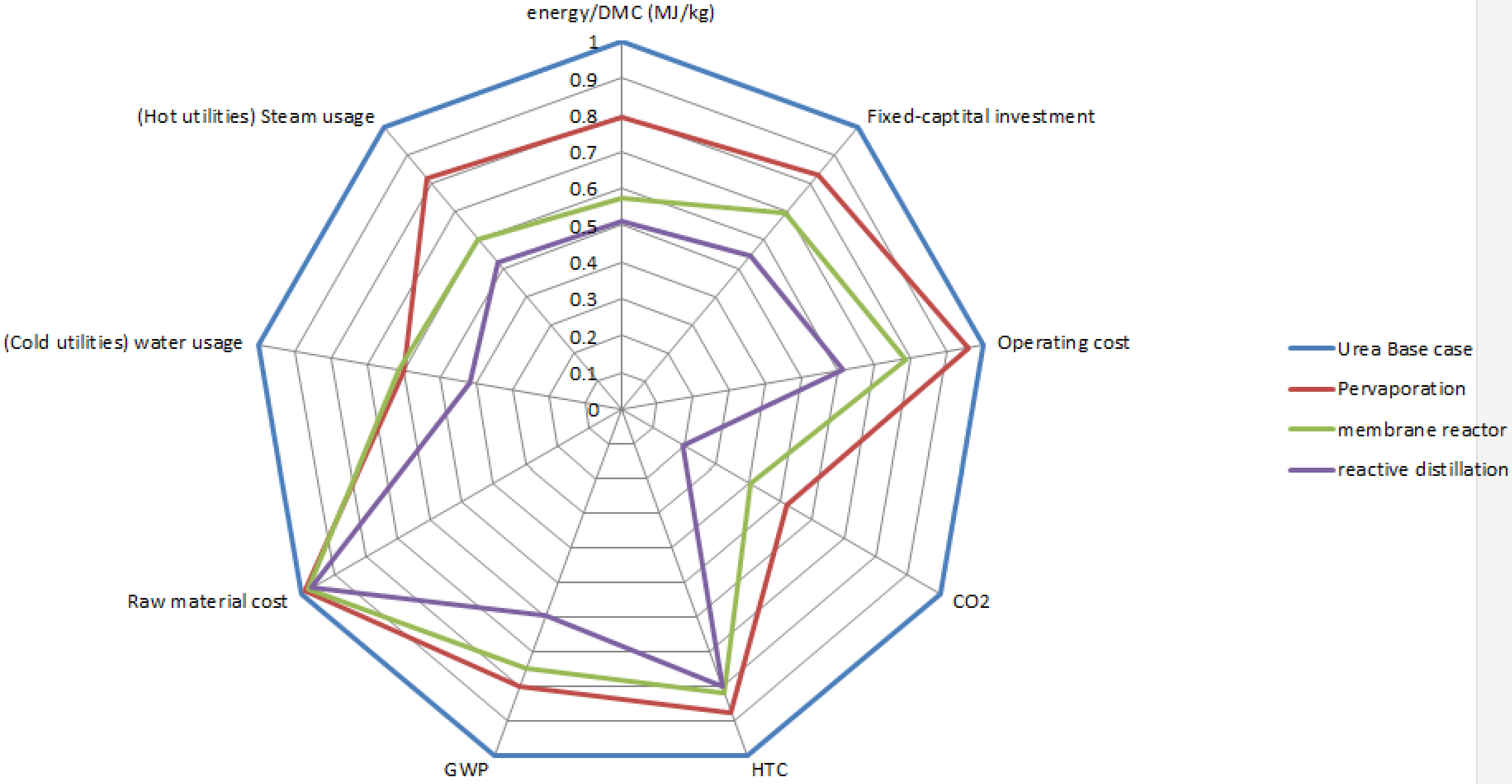
CO2 Recovery	Exit CO2 conc. [molar fraction]	Overall CO2 capture [%]	Utility cost [$/yr]	Capital investment [$]	Indirect carbon emission [g CO2 equivalent/kWh]	Carbon footprint [g CO2 equivalent/kWh]
High Purity	0.9988	99.98	$9,823,289.00	$3,840,304.44	90.5	76.4
Low Purity	0.9744	99.65	$1,163,417.00	$4,446,596.33	9.94	-4.2

Redesign of a CO2 conversion process



Kongpanna et al. 2014, Fjellerup et al. 2015

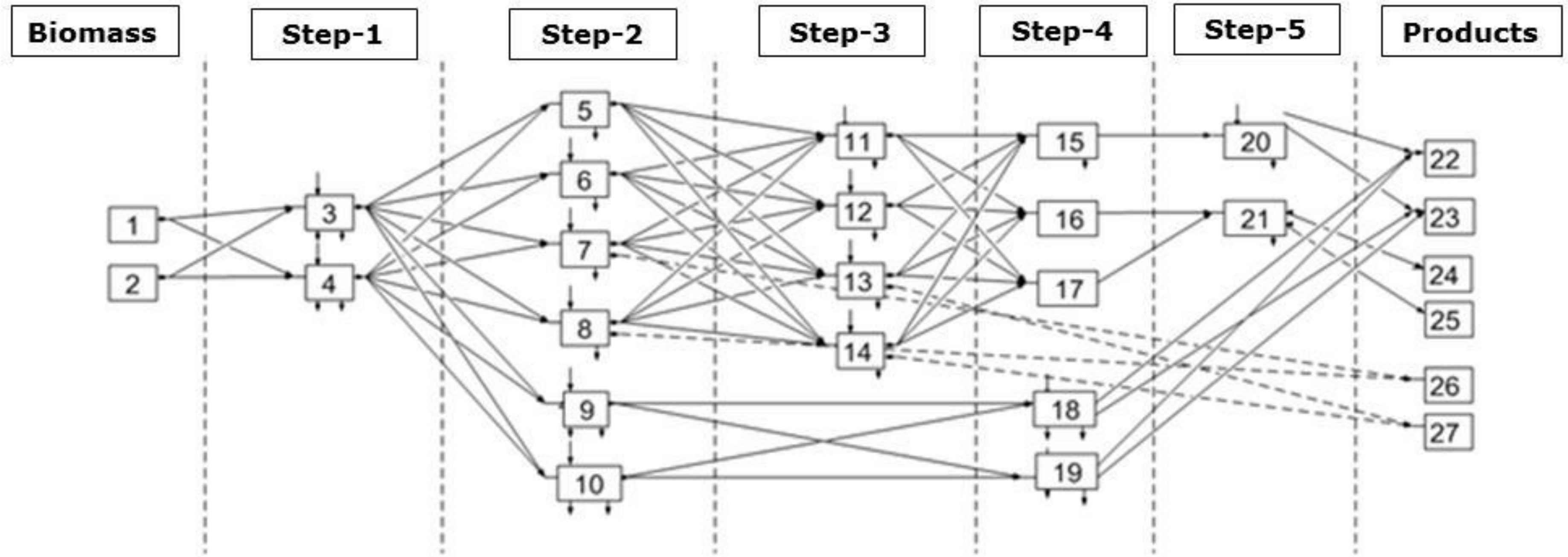
Production of block chemicals through CO2 conversion



Kongpanna et al. 2014

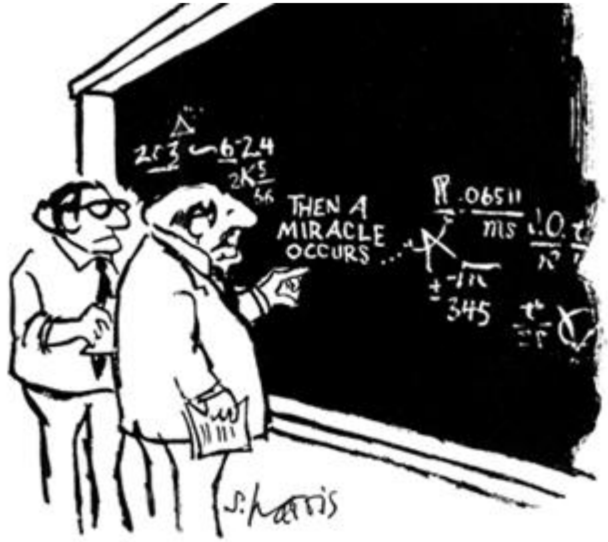
Tailor-made biochemicals (biorefinery)

OBJECTIVE : Develop a systematic method and associated tools that can analyze and design innovative biorefinery networks based on chemical and biological approaches to convert biomass feedstock into valuable chemicals and biofuels.



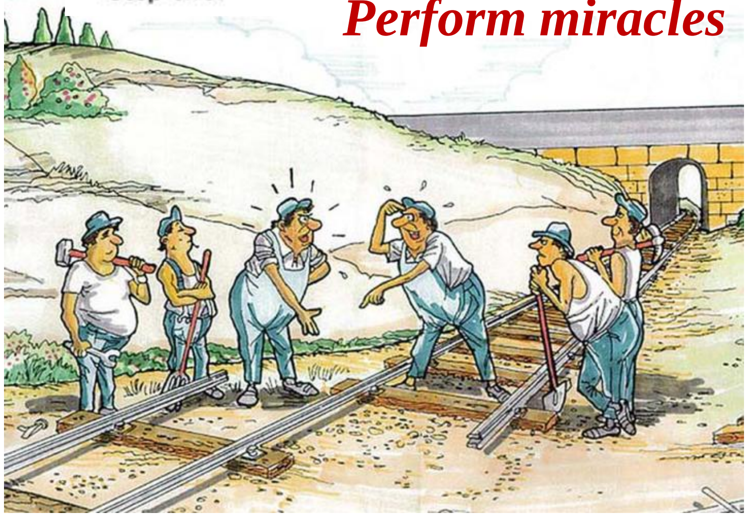
Partners: **Chemical & Biomolecular Engineering, KAIST (plus research groups from USA, Brazil, China, Thailand, Mexico)**

Something more to think about!



“I think you should be more explicit here in step two.”

Perform miracles



Provide reliable solution

Avoid drinking from the water-hose

"IF WE CHANGE ONE MOLECULE OF THIS PAIN-KILLER, WE'LL GET AN EXCELLENT HAIR SPRAY. THE SALES PEOPLE ARE DECIDING WHICH WAY TO GO."

We must decide!

Concluding Remarks

- **It is possible to find new innovative solutions**
- **Issues related to uncertainty of data & models are important and need to be considered**
- **Mutlidisciplinary nature of problems need to be handled**
- ***A good understanding of the problem is necessary***
- ***Identify the best solution strategy***
- ***Efficiency and reliability of the solution is very important***
- ***First identify and reduce the search space with model-based techniques and then use focused experiments to determine the final solution***

- **Golden Era for Chemical Engineering (Westmoreland, 2014) – do something!**
- **Focused team-effort needed to meet the challenges**
- **Join forces and seek global solution strategies**

The PSE for SPEED Project

Olivia Perederic; Fang Zhou; Alberto Orsi; Erki Kikas plus visitors (Thailand, China, indonesia)