Lecture 11: Sustainability analysis

1. Sustainability Analysis
    A. Introduction to Environmental Impact Analysis
    B. Sustainability metrics
    C. Safety index
    D. Sustainable process design

Additonal notes (own reading)

1. Reactor Design & Analysis
2. Introduction to Mass Integration

Sustainability Analysis

Ana Carvalho, Rafiqul Gani, Henrique Matos, “Design of sustainable chemical processes: Systematic retrofit analysis generation and evaluation of alternatives”, *Process Safety and Environmental Protection,* 86(5), 328-346, 2008

Ana Carvalho, Henrique A. Matos, Rafiqul Gani, “SustainPro - A tool for systematic process analysis, generation and evaluation of sustainable design alternatives”, *Computers & Chemical Engineering*, 50, 8-27, 2013

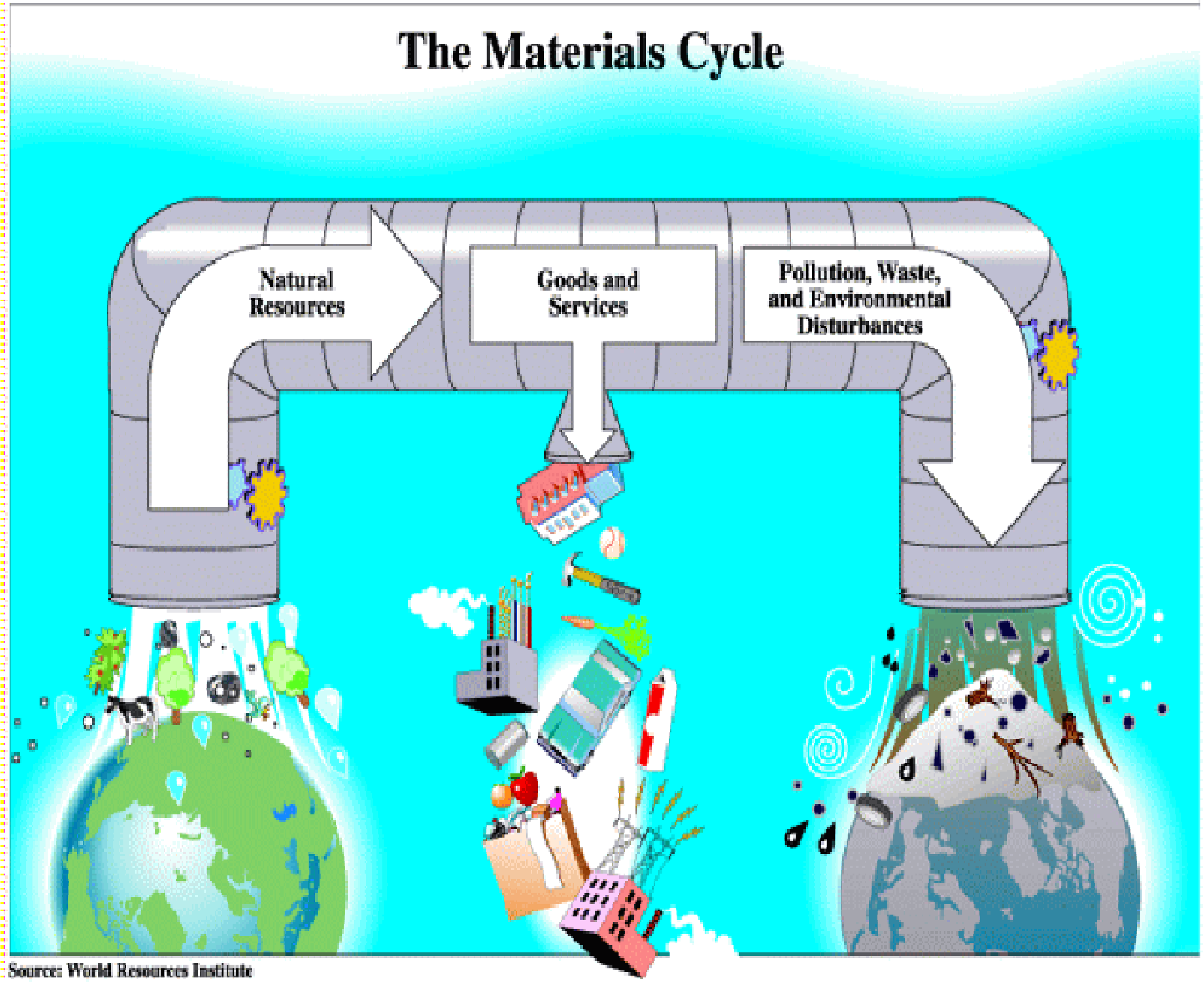
Why worry about waste reduction?

Are our products & processes sustainable?

Only 25 wt% of what goes into the pipe comes out as goods and services

Scope for much more (40% or more) improvement needed

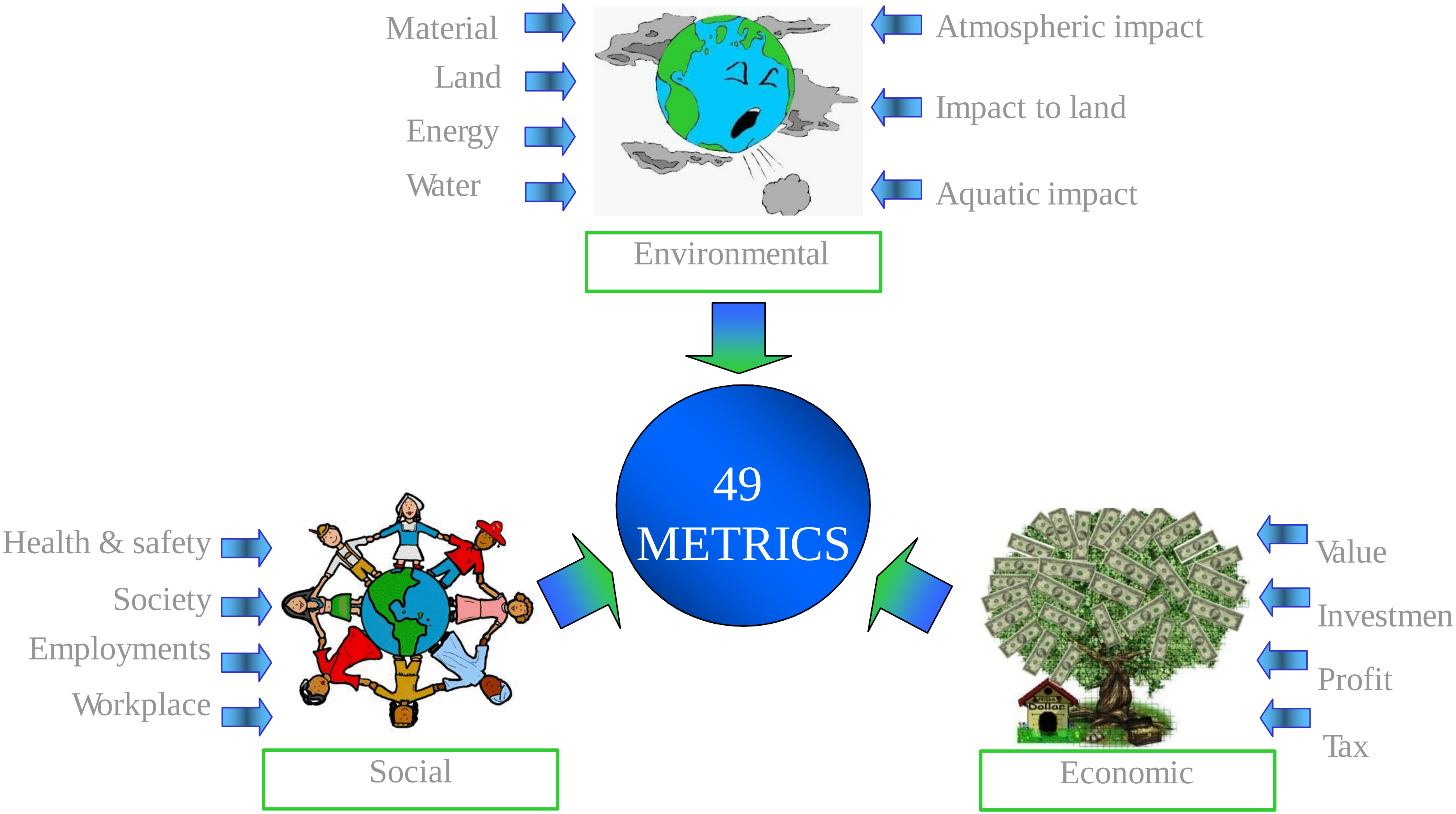
Adapted from Driolli, 2005



Source: World Resources Institute

Without signficant improvements, our products-processes will not be sustainable

Model for Sustainability Analysis



Material
Land
Energy
Water

Atmospheric impact
Impact to land
Aquatic impact

Environmental

49
METRICS

Health & safety
Society
Employments
Workplace

Social

Value
Investmen
Profit
Tax

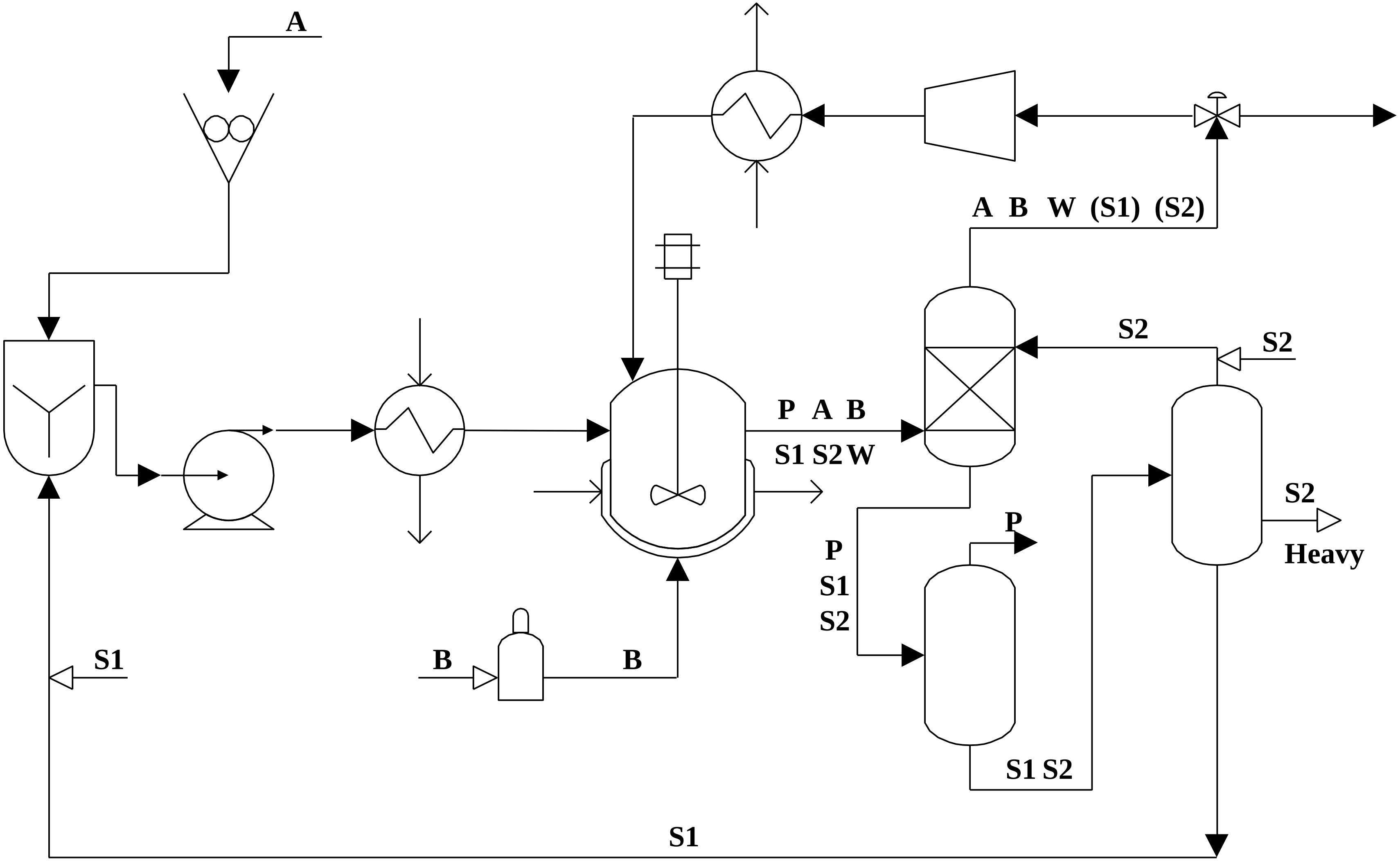
Economic

Azapagic , *Sustainable Development Progress Metrics*, IChemE Sustainable Development Working Group, IChemE, Rugby, UK, 2002;

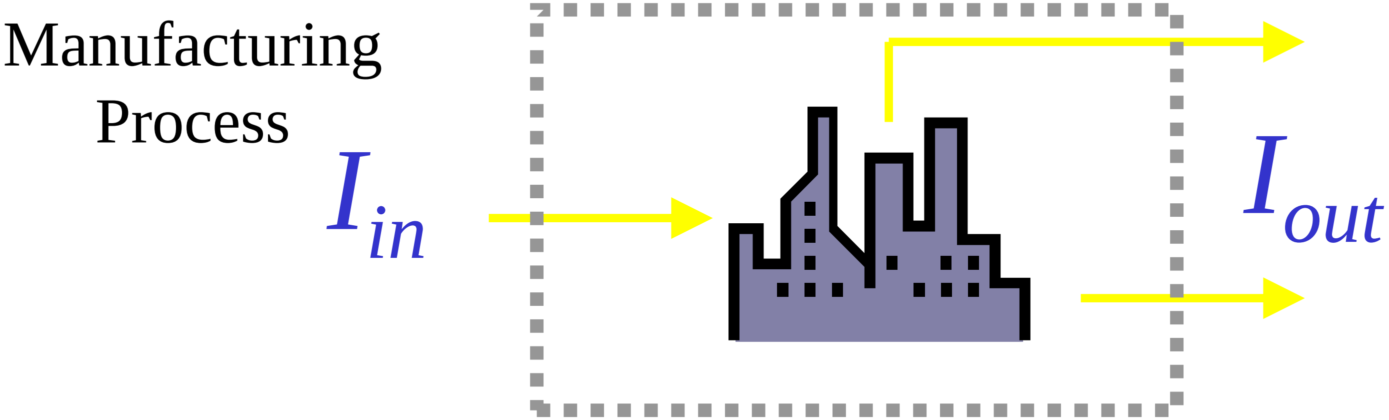
A. Environmental Impact Analysis: The WAR Algorithm

Raymond Smith, Douglas Young, Jennifer Saxe
U.S. Environmental Protection Agency
National Risk Management Research Laboratory
26 W. Martin Luther King Drive
Cincinnati, OH 45268 USA

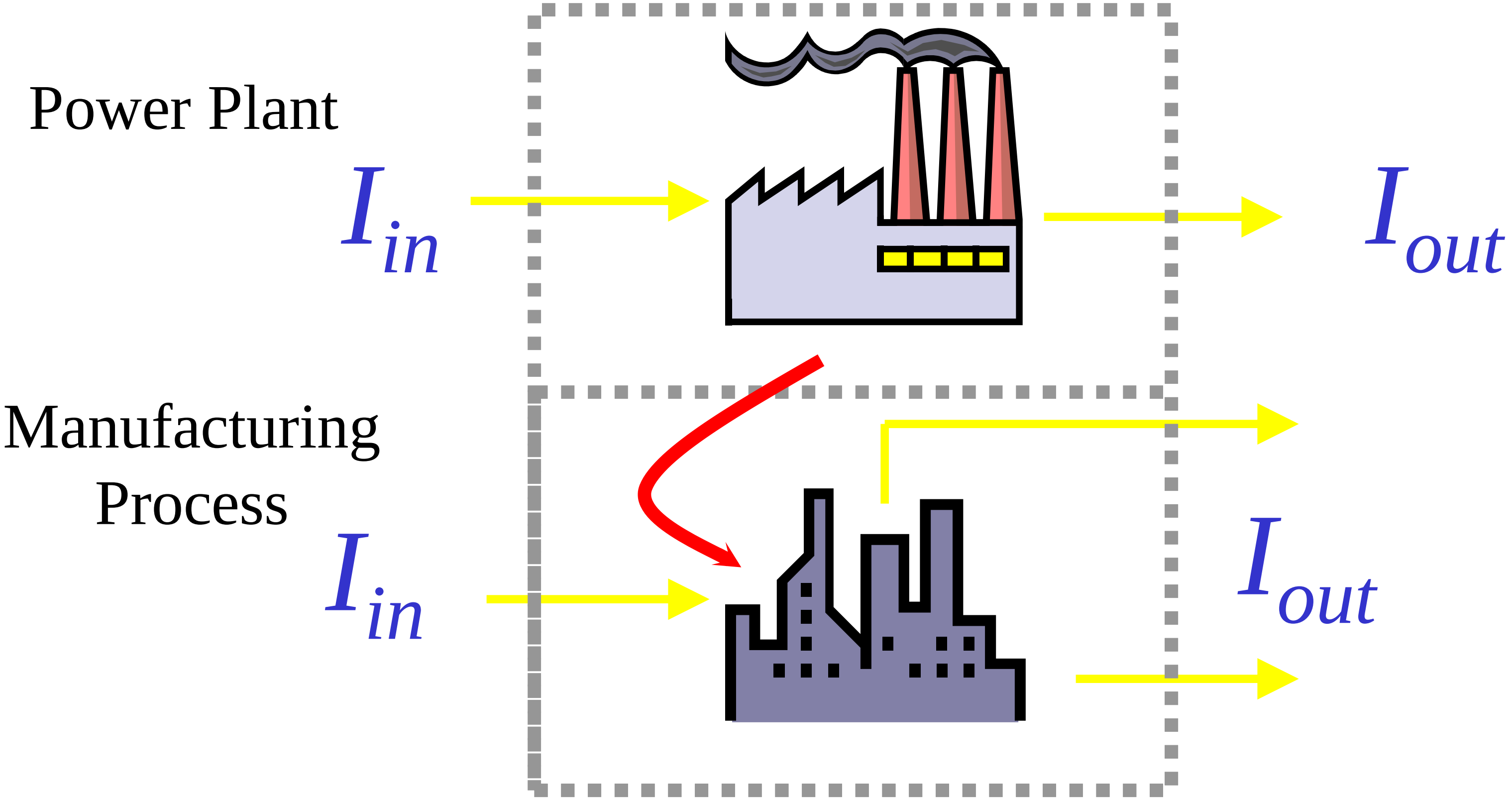
Evaluating Chemical Processes



Waste Reduction (WAR) Algorithm



Waste Reduction (WAR) Algorithm



Power Plant

I_{in}

I_{out}

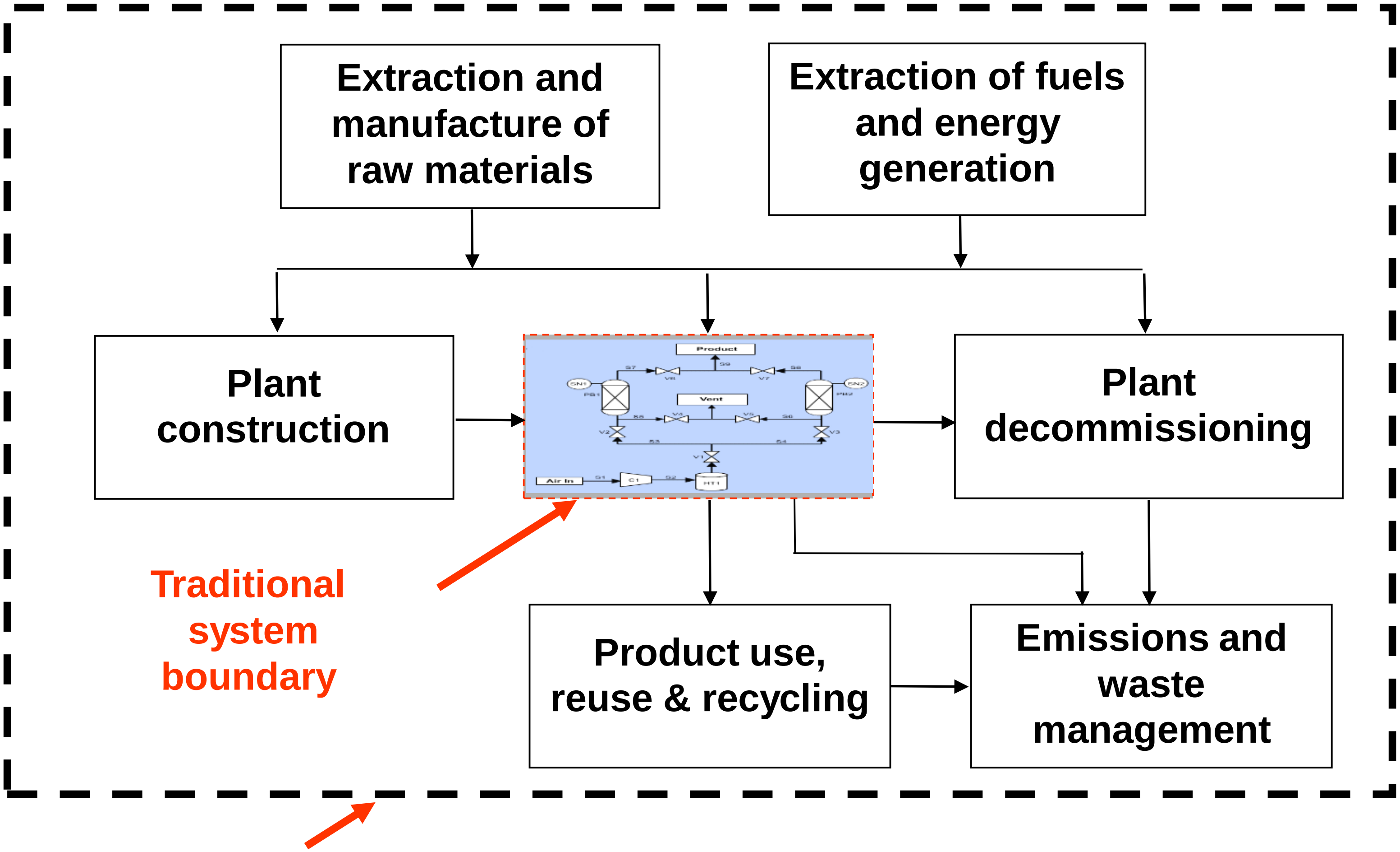
Manufacturing Process

I_{in}

I_{out}

Waste Reduction (WAR) Algorithm

SYSTEM (from 'cradle to grave')



Extraction and manufacture of raw materials

Extraction of fuels and energy generation

Plant construction

Plant decommissioning

Traditional system boundary

Product use, reuse & recycling

Emissions and waste management

New system boundary

At steady state

$$0 = I_{in} - I_{out} + I_{gen}$$

Fundamental equation of the WAR Algorithm

Units are in PEI/time

Potential Environmental Impact (PEI)

$$I = \sum_i \alpha_i \sum_j M_j \psi_{ij}$$

α_i = weighting factor for impact category *i*

M_j = mass flow rate of chemical *j* (mass/time)

ψ_{ij} = chemical and category specific impact (PEI/mass)

Impact Categories in WAR

- Human Toxicity Potential by Ingestion
- Human Toxicity Potential by Dermal/Inhalation Exposure
- Aquatic Toxicity Potential
- Terrestrial Toxicity Potential
- Acidification Potential
- Photochemical Oxidation Potential
- Global Warming Potential
- Ozone Depletion Potential

Use of WAR through ICAS: Follow the instructions given in the ICAS-PA-Examples.pdf file)

Other Impact Categories

- Acute, Chronic and Carcinogenic Effects Combined into a Single Category…

  …for what time period?
- Presenting (Midpoint) Category Indicators for Human Health on the Basis of Disability Adjusted Life Years
- Resource Depletion – Use of Different Forms of Mass/Energy
- Renewable vs. Non-renewable Resources

Number of Chemicals

From 1600 to a New Database of Approximately 5000

Example Databases Used in WAR:

- Hazardous Substance DataBase
- National Toxicity Program
- Registry of Toxic Effects and Chemical Substances
- AQUatic toxicity Information and REtrieval
- Intergovernmental Panel on Climate Change
- World Meteorological Organization

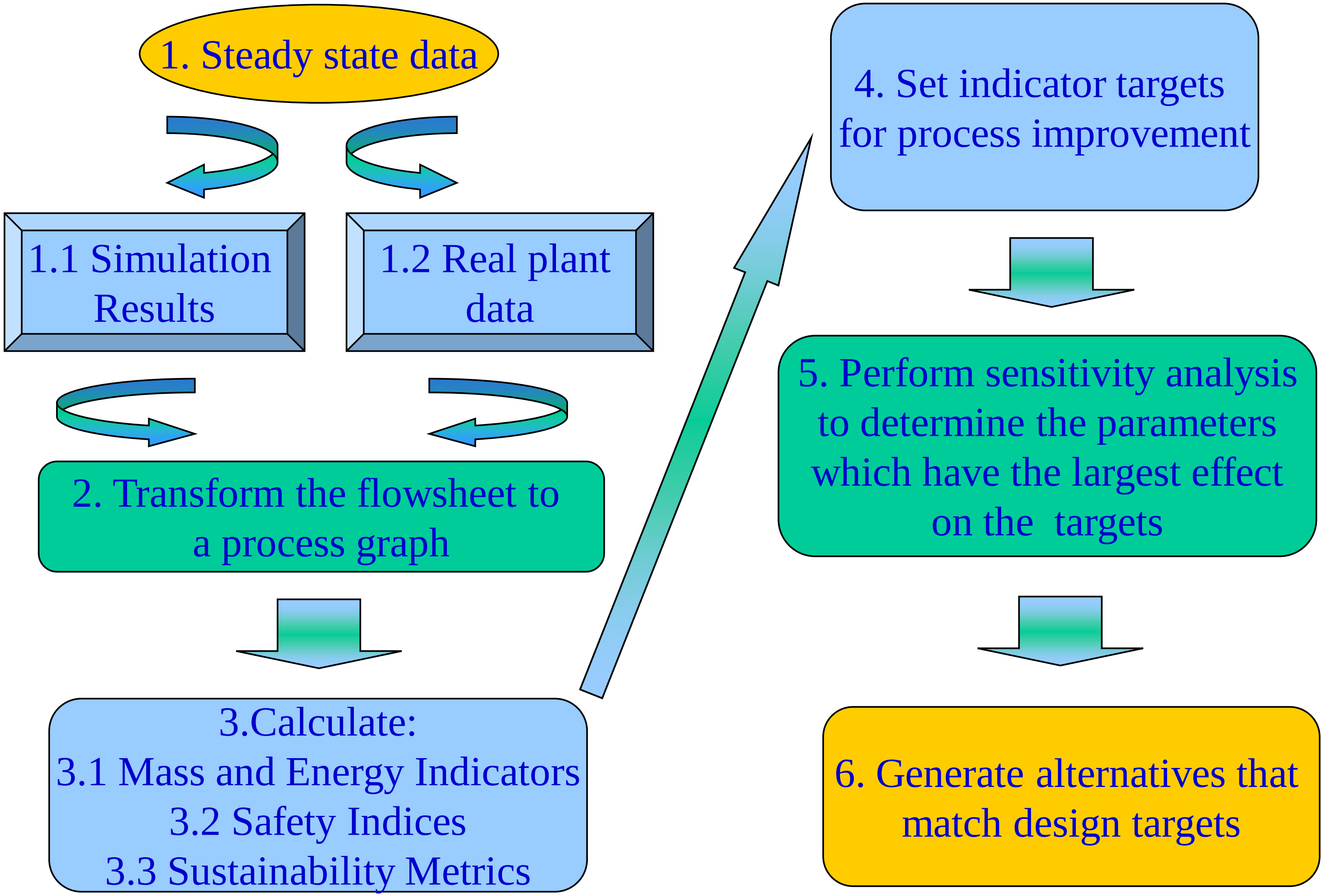
B. Sustainability Metrics

- Metrics proposed by IChemE (see slide 30 – also see document in Campus-net)
- Metrics proposed by AIChE
- others

C. Health & Safety Index

- Inherent chemical index (0-4 score; total 27)
- Inherent process index (0-4 score; total 28)

D. Method for sustainable process design



1. Steady state data

1.1 Simulation Results

1.2 Real plant data

2. Transform the flowsheet to a process graph

3.Calculate:
3.1 Mass and Energy Indicators
3.2 Safety Indices
3.3 Sustainability Metrics

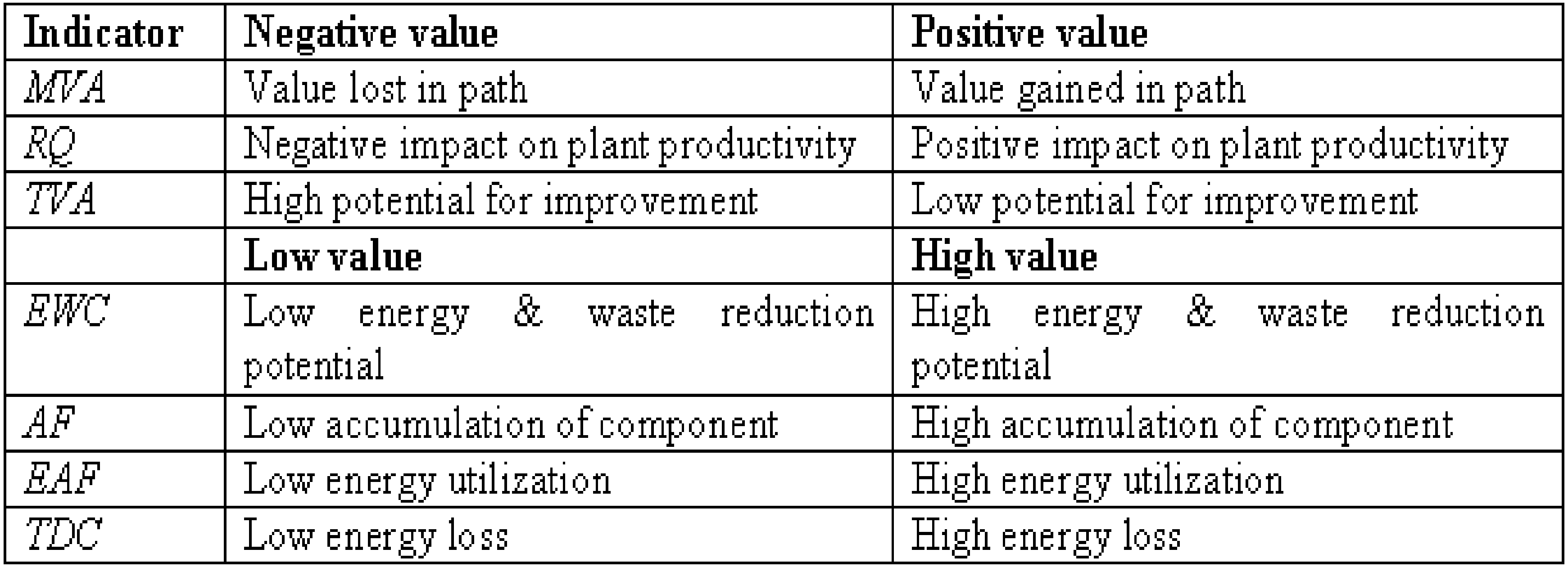
4. Set indicator targets for process improvement

5. Perform sensitivity analysis to determine the parameters which have the largest effect on the targets

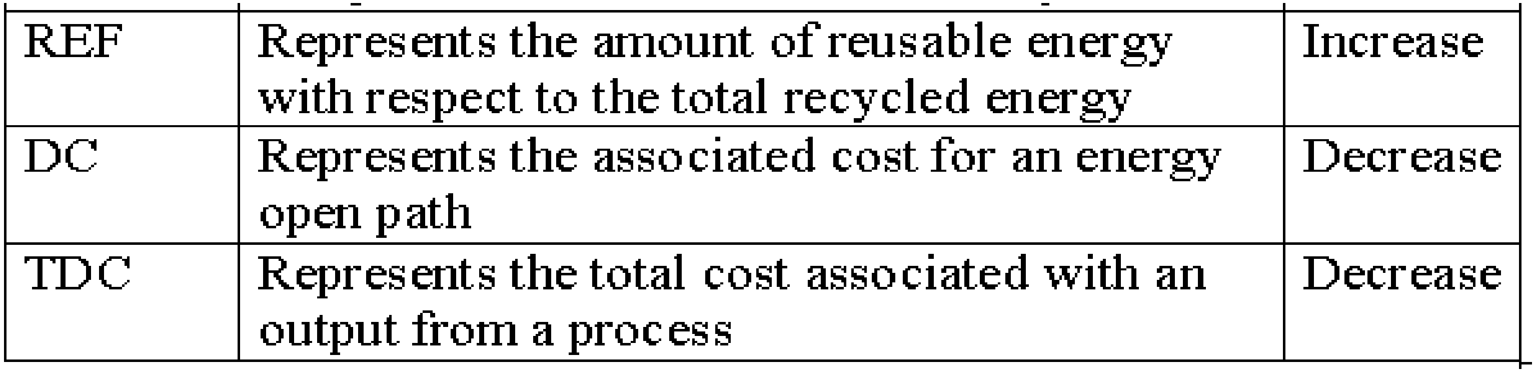
6. Generate alternatives that match design targets

Analysis of Indicators

Identify the target indicators

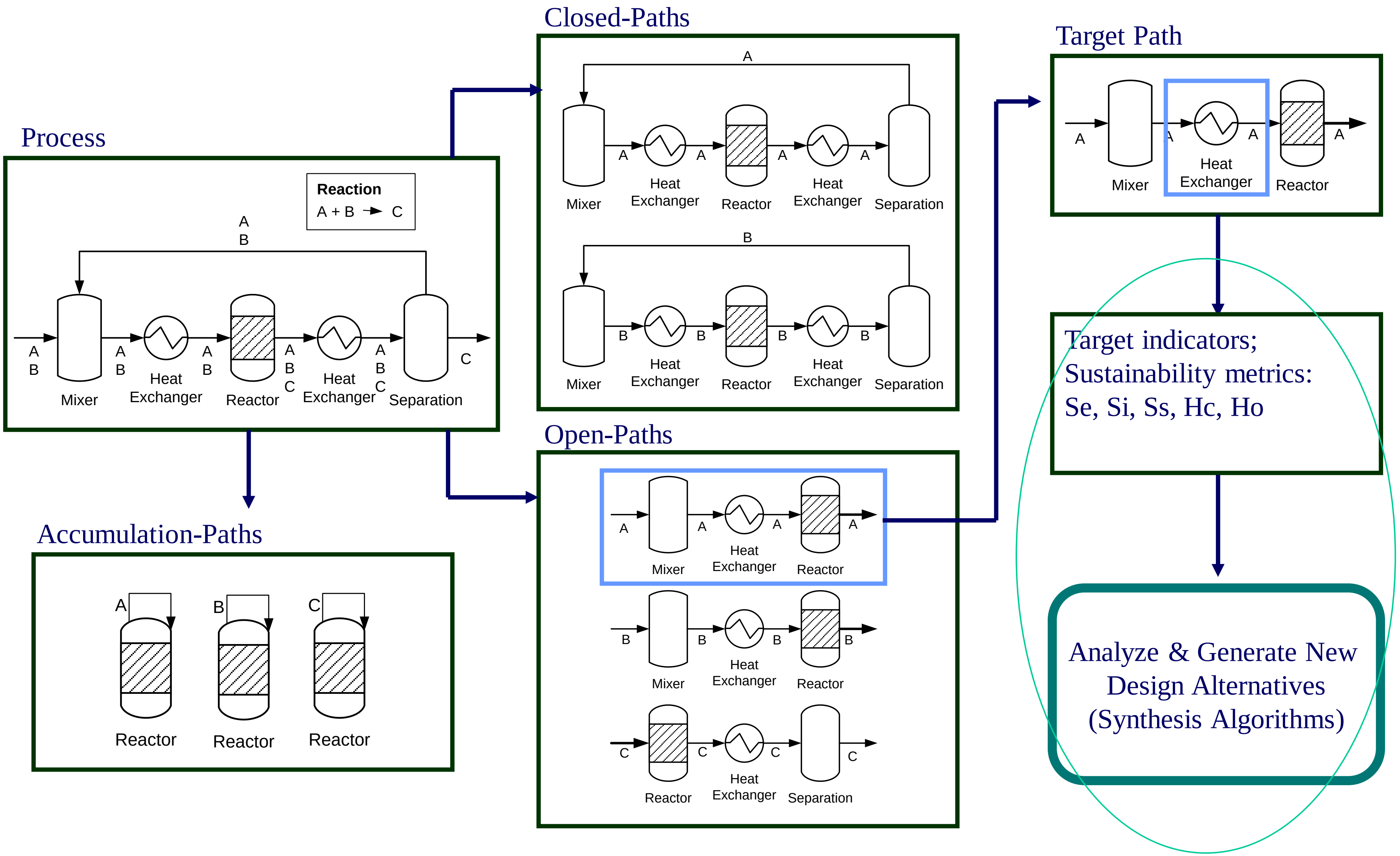


Indicator	Negative value	Positive value
MVA	Value lost in path	Value gained in path
RQ	Negative impact on plant productivity	Positive impact on plant productivity
TVA	High potential for improvement	Low potential for improvement
	Low value	**High value**
EWC	Low energy & waste reduction potential	High energy & waste reduction potential
AF	Low accumulation of component	High accumulation of component
EAF	Low energy utilization	High energy utilization
TDC	Low energy loss	High energy loss



REF	Represents the amount of reusable energy with respect to the total recycled energy	Increase
DC	Represents the associated cost for an energy open path	Decrease
TDC	Represents the total cost associated with an output from a process	Decrease

Overview of method

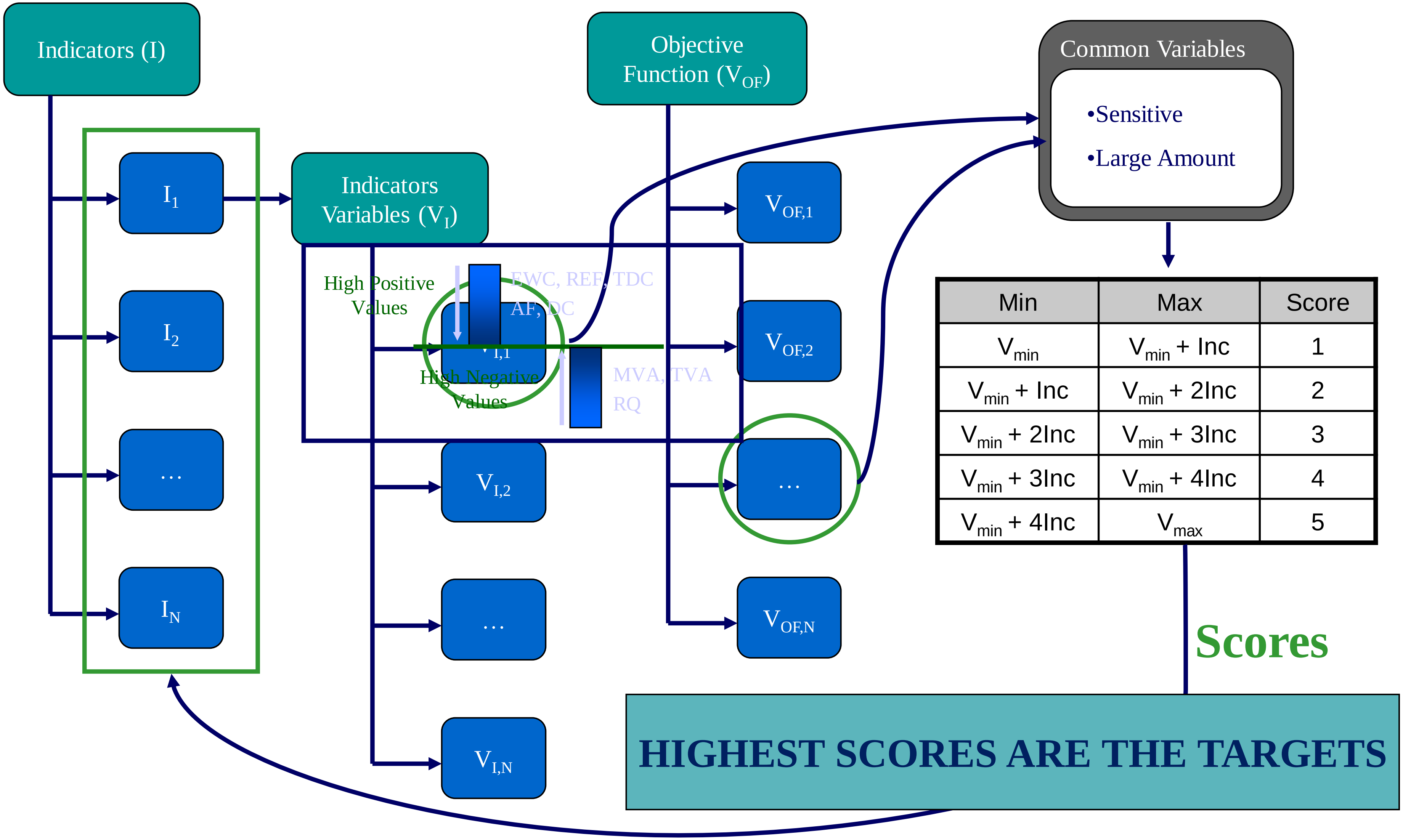


Target indicators;
Sustainability metrics:
Se, Si, Ss, Hc, Ho

Analyze & Generate New Design Alternatives (Synthesis Algorithms)

Defining targets for improvement

Indicators – variables - objective



Indicators (I)

I_1

I_2

…

I_N

Indicators Variables (V_I)

High Positive Values

EWC, REF, TDC

AF, DC

$V_{I,1}$

High Negative Values

MVA, TVA

RQ

$V_{I,2}$

…

$V_{I,N}$

Objective Function (V_{OF})

$V_{OF,1}$

$V_{OF,2}$

…

$V_{OF,N}$

Common Variables

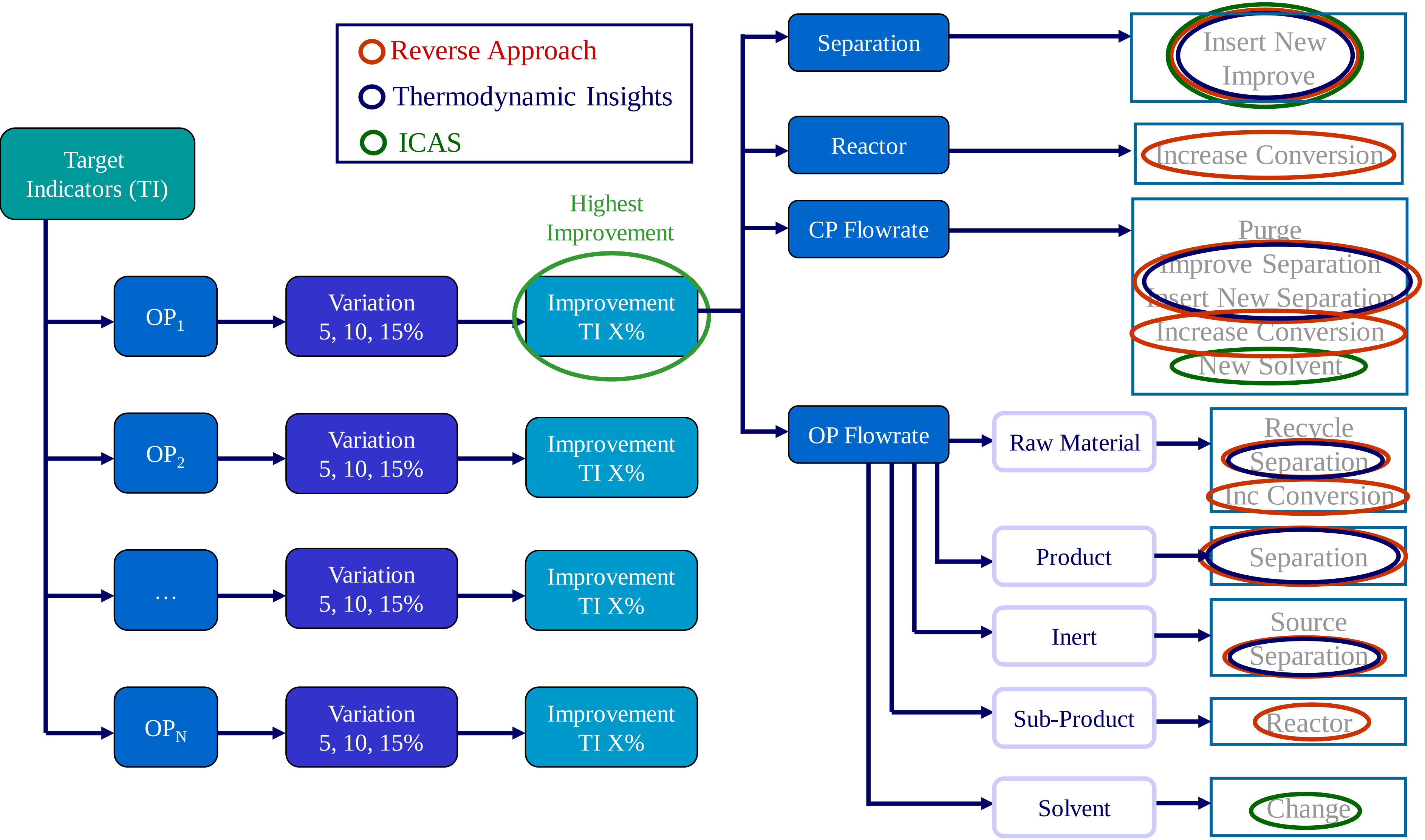
- Sensitive
- Large Amount

Min	Max	Score
V_{min}	V_{min} + Inc	1
V_{min} + Inc	V_{min} + 2Inc	2
V_{min} + 2Inc	V_{min} + 3Inc	3
V_{min} + 3Inc	V_{min} + 4Inc	4
V_{min} + 4Inc	V_{max}	5

Scores

HIGHEST SCORES ARE THE TARGETS

Generate sustainable design alternatives



○ Reverse Approach
○ Thermodynamic Insights
○ ICAS

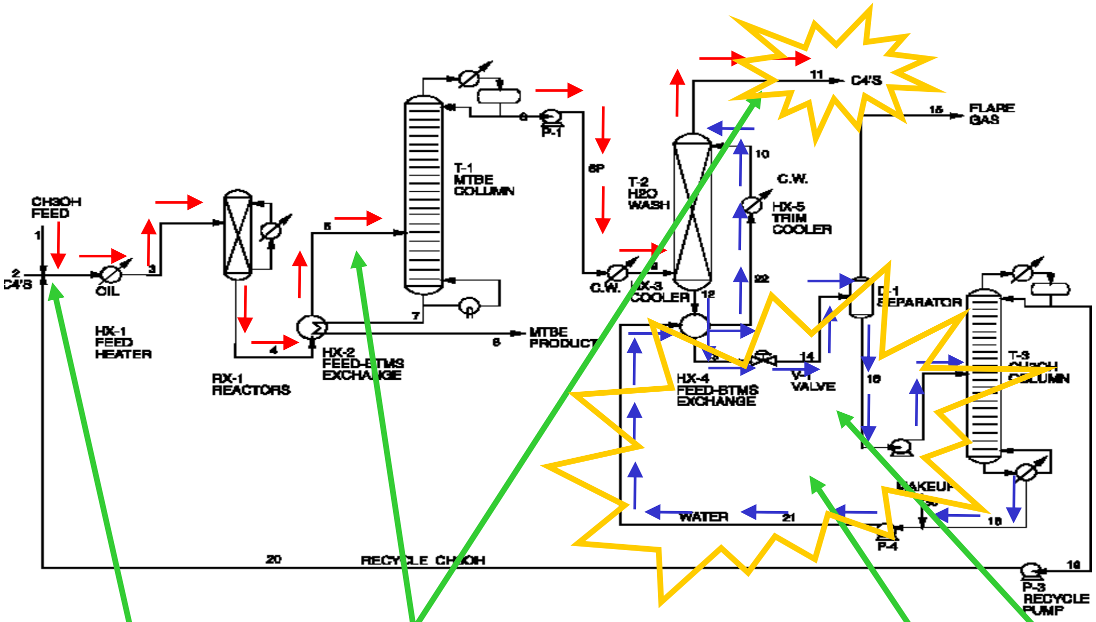
Target Indicators (TI)

OP_1 → Variation 5, 10, 15% → Improvement TI X%
OP_2 → Variation 5, 10, 15% → Improvement TI X%
… → Variation 5, 10, 15% → Improvement TI X%
OP_N → Variation 5, 10, 15% → Improvement TI X%

Highest Improvement

Separation → Insert New, Improve
Reactor → Increase Conversion
CP Flowrate → Purge, Improve Separation, Insert New Separation, Increase Conversion, New Solvent
OP Flowrate
- Raw Material → Recycle, Separation, Inc Conversion
- Product → Separation
- Inert → Source, Separation
- Sub-Product → Reactor
- Solvent → Change

Application Example: MTBE Process

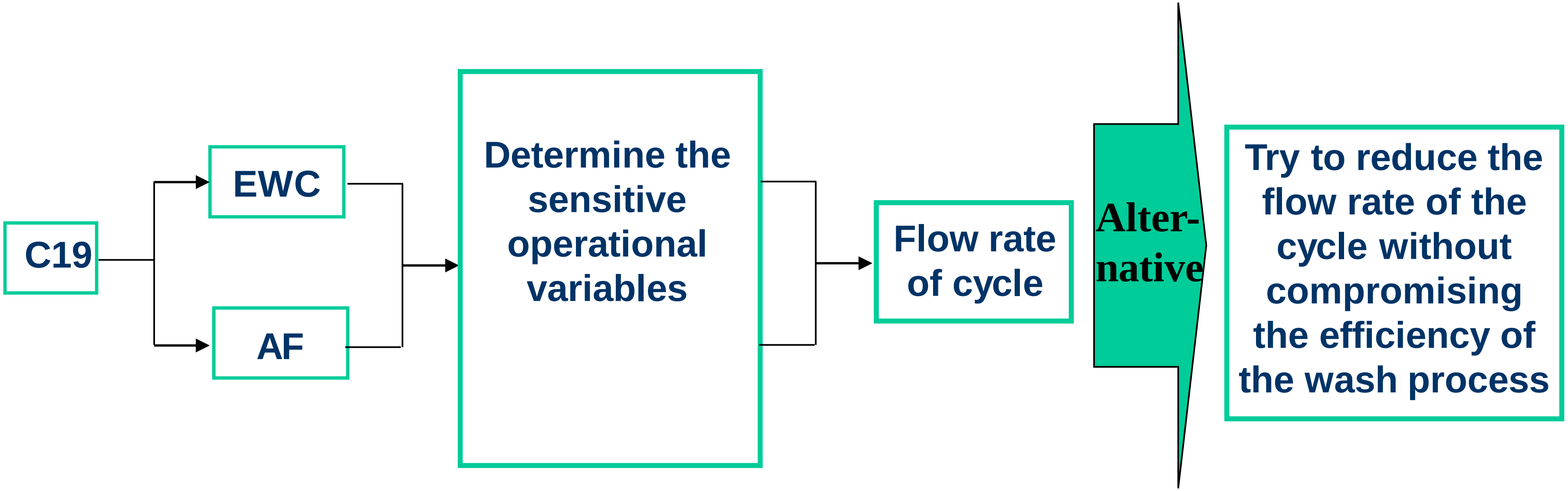


Open path	Component	MVA (10³ $/y)	EWC (10³ $/y)
O7	n-butane	-376.41	9.07
O9	Isobutane	-1714.78	260.70
O11	1 Butene	-282.62	43.41
O14	BTC2/BTT2	-403.74	63.91

Closed path	Component	AF	EWC (10³ $/y)
C19	Water	626.51	313.35

Application Example: MTBE Process

- **Energy, water, material, environmental impact and economic metrics**
  Total metrics= 23
- **Safety index = 30**
- **Through an algorithm determinations of the indicators which have more influence in the profit- Cycle path C19**



C19

EWC

AF

Determine the sensitive operational variables

Flow rate of cycle

Alter-native

Try to reduce the flow rate of the cycle without compromising the efficiency of the wash process

Generate (design) process alternatives

Results of the sensitivity analysis

A set of indicators; their target values; the process variables that can be changed to achieve the target; the sustainability metrics that would be affected; the environmental impact factors that would be affected; the safety factors that would be affected

→

Each set of changed process variables corresponds to a generated sustainable process alternative

Application Example: MTBE Process

Reduce 20% water in recycle

↔ Constant efficiency 99.9 % (methanol, water)

↑ 14.4 % and 20.0 % reduction of AF, and EWC

↓ Insignificant increase MVA values for paths O3, O4, O5, O9, O13 and O18

↔ Safety Index constant

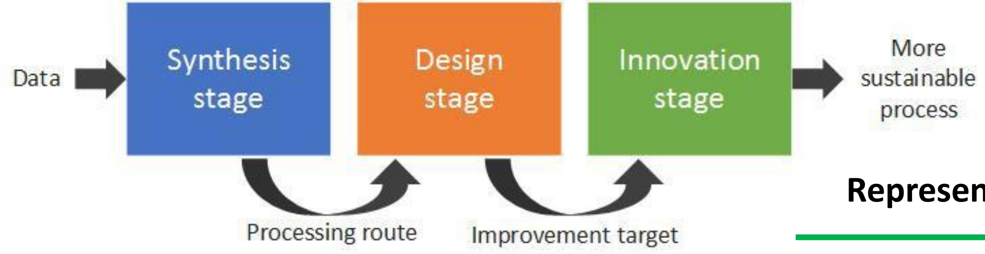
↑ Energy and water sustainability metrics decrease 3% and 4 %

↔ Global impact almost constant

↑ Gross margin increase 1.6%, but the increase in the profit will be greater due to the reduction in investment costs

SPEED

Sustainable process synthesis-design-intensification

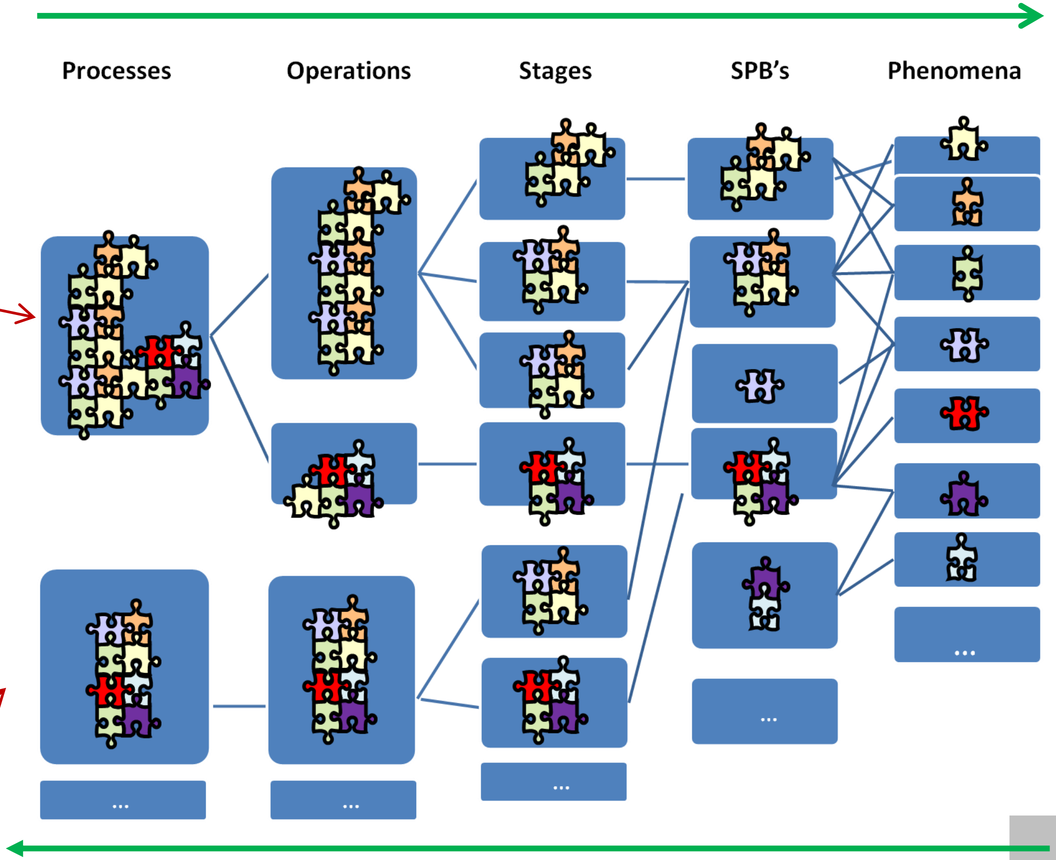


CACE, PI-special issue, 2017; CACE, 81, 2015)

Intensification method:

Starting with a base case design (synthesis stage), set targets for improvement (design stage), generate new intensified options that match design targets and make the process more sustainable (innovation stage)

Represent base case process wrt to operations to phenomena

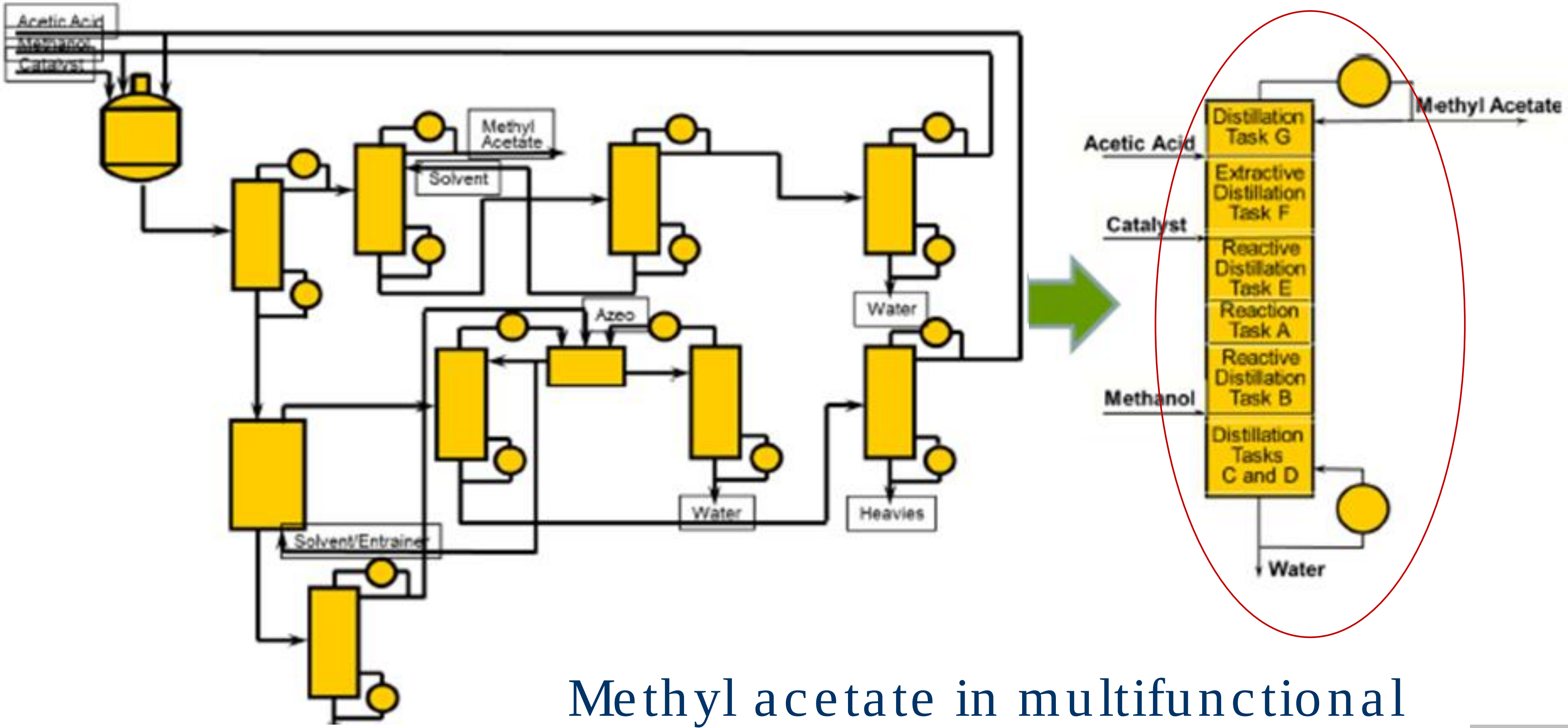


Recombine the phenomena to generate new intensified options

SPEED

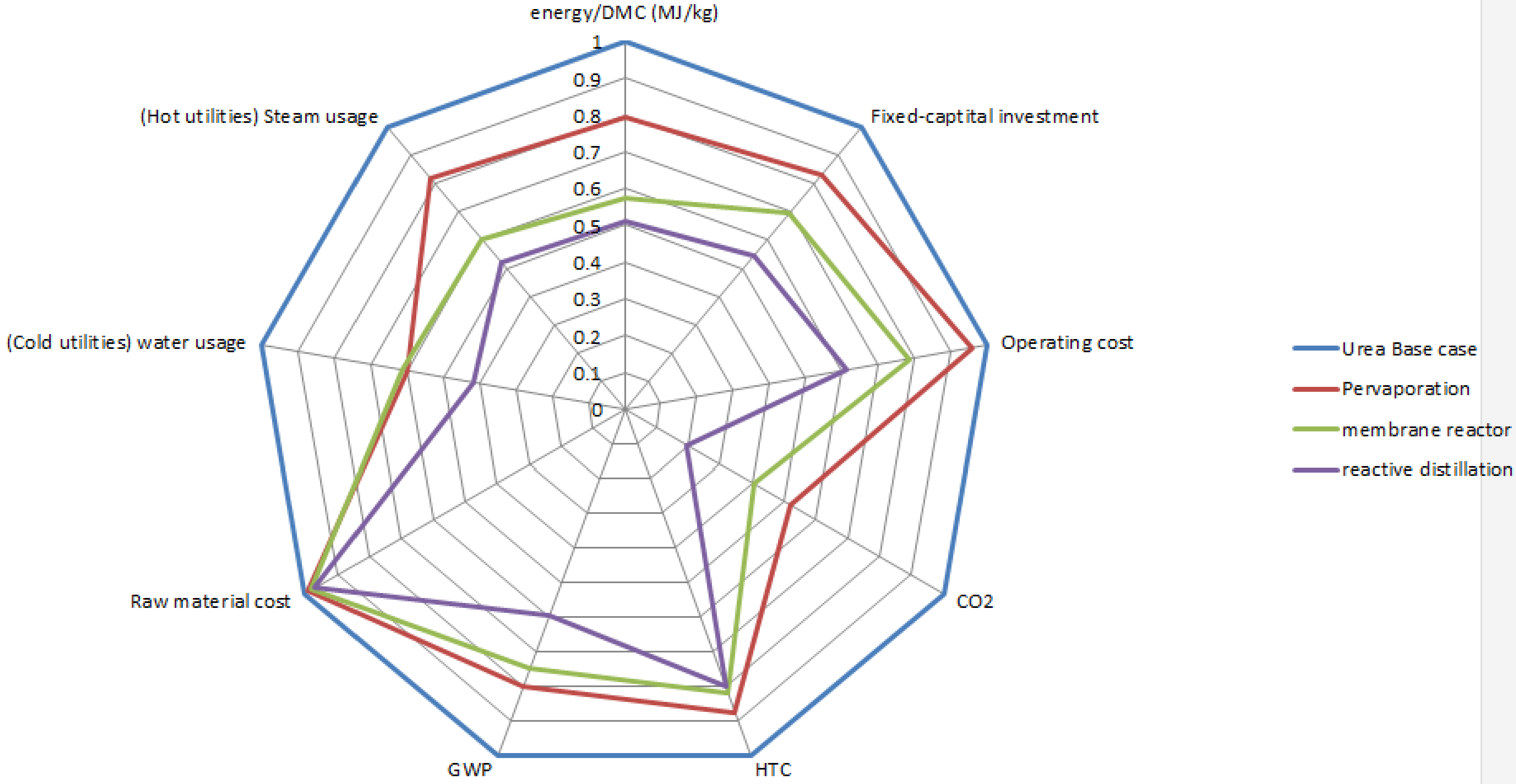
Find innovative solutions

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



Methyl acetate in multifunctional reactor (Eastman Chemicals)

Production of block chemicals through CO2 conversion

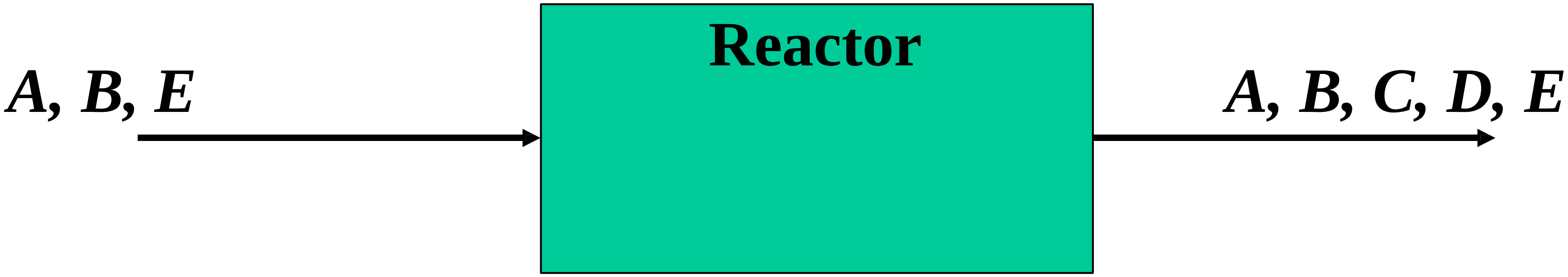


Kongpanna et al. 2014

Design problem final conclusions (add these numbers as conclusions of your design)

- Amount (Kg) of product s (main) per Kg of raw materials
- Cost of products per Kg of raw materials
- Amount of energy (steam) used per kg of product
- Amount of energy (electricity) per Kg of product
- Amount of water per Kg of product
- Amount of waste per Kg of product
- Atom efficiency = (atoms in main product)/(total atoms in raw materials)

Reactor Design & Analysis
(Chapter 13 of textbook)



A + B = C + D

Design Issues: Type of reactor; number of reactor; reactor design parameters (temperature, pressure, conversion, kinetic-equilibrium, volume, residence time, ….)

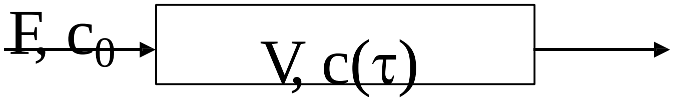
Basic Steps in Reactor Design & Analysis

- Write reactions
- Find data for the reaction (conversion, kinetic model, catalyst, …)
- Write appropriate models for CSTR, Plug-Flow & Recycle-Reactors
  - Reaction rate model
  - Use kinetic or equilibrium model to fix T, P
  - Determine required reactor volume
  - Residence time
- Verify design decisions through simulation

Basic Steps in Reactor Design & Analysis

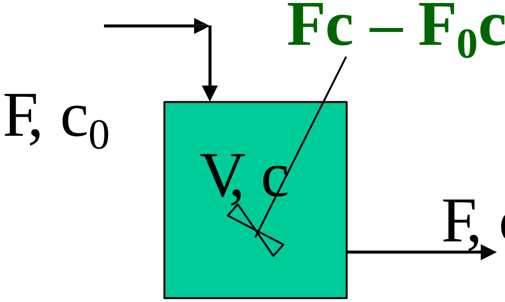
- **Write reactions** $A = B = C$ **(all reversible reactions)**
- **Write (simple) models for CSTR, Plug-Flow & Recycle-Reactors**

$$d(Fc)/dV = r(c);\ c(0) = c_0$$

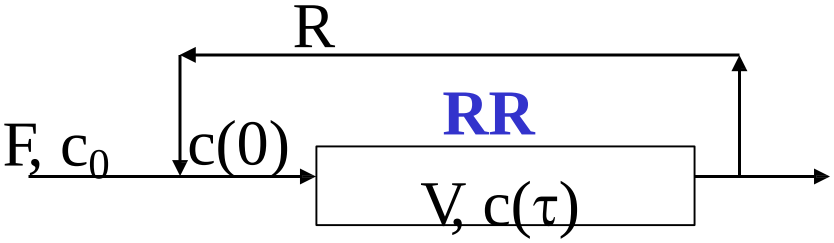


PFR

$$Fc - F_0c_0 = Vr(c)$$



CSTR



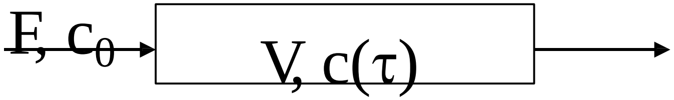
$$d(Fc)/dV = r(c)$$

$$c(0) = (RF_Vc_V + F_0c_0)/\ (RF_V+1)$$

Basic Steps in Reactor Design & Analysis

$$d(Fc)/dV = r(c);\ c(0) = c_0$$

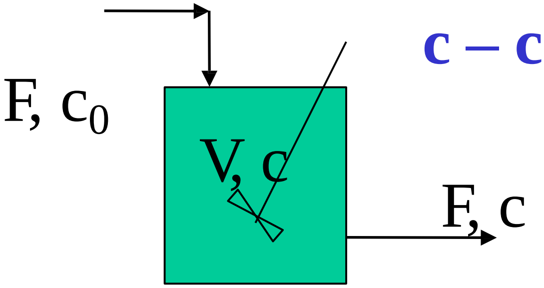
$$dc/d\tau = r(c)$$



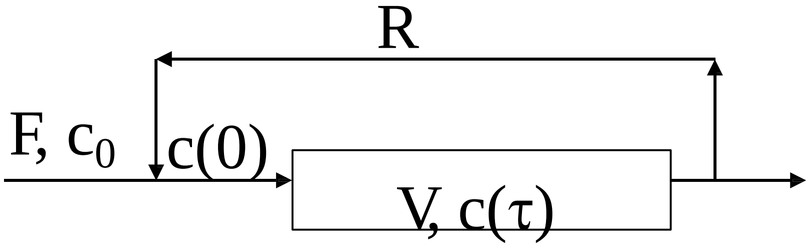
PFR

$$Fc - F_0c_0 = Vr(c)$$

$$c - c_0 = r(c)$$



CSTR



RR

$$d(Fc)/dV = r(c)$$

$$c(0) = (RF_Vc_V + F_0c_0)/(RF_V+1)$$

$$(R+1)dc/d\tau = r(c)$$

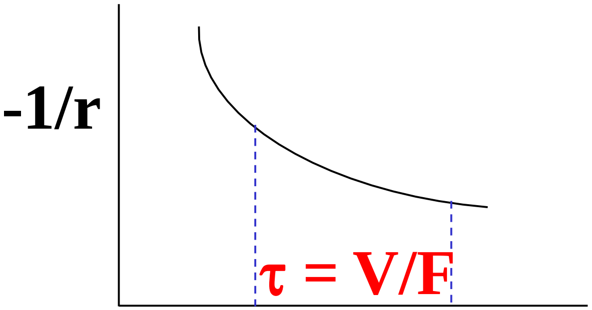
$$c(0) = (Rc_V + c_0)/(R+1)$$

Note: $\tau = V/F$

Basic Steps in Reactor Design & Analysis

$d(Fc)/dV = r(c); \; c(0) = c_0$

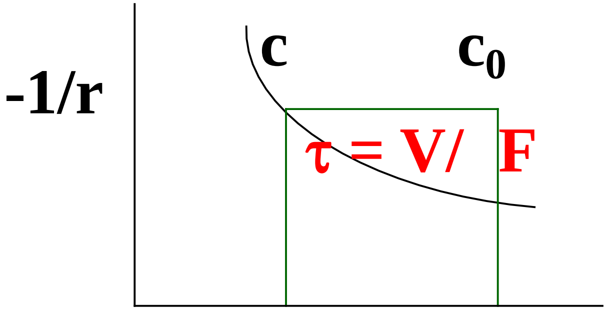
$dc/d\tau = r(c)$



PFR

$Fc - F_0c_0 = Vr(c)$

$c - c_0 = r(c)$



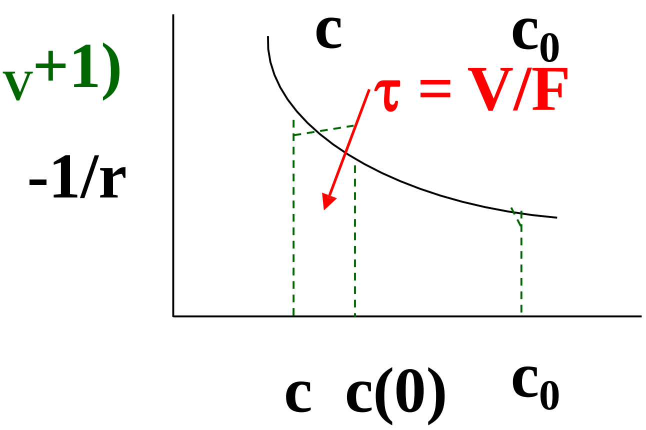
CSTR

$d(Fc)/dV = r(c)$

$c(0) = (RF_Vc_V + F_0c_0)/(RF_V+1)$

$(R+1)dc/d\tau = r(c)$

$c(0) = (Rc_V + c_0)/(R+1)$

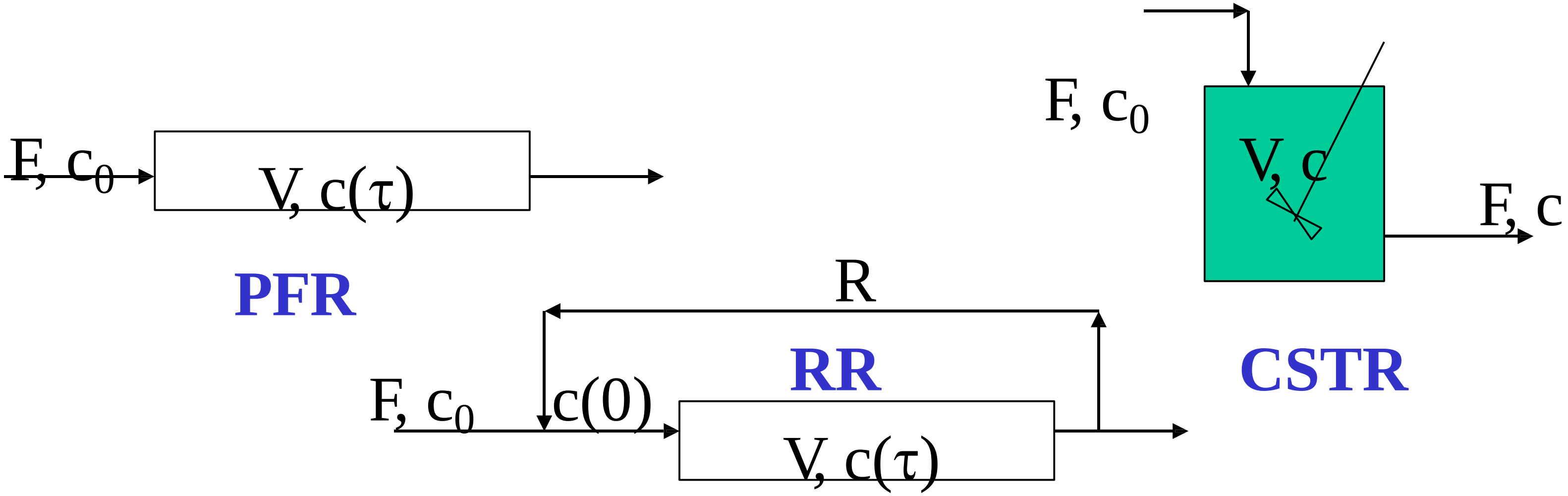


RR

Basic Steps in Reactor Design & Analysis

* **Write reactions** **A = B = C (all reversible reactions)**

***Write simple models for CSTR, Plug-Flow & Recycle-Reactors**



***Find data for the reaction (conversion, kinetic model, catalyst, …) – Depending on the values of F, V, τ, conversion, decide the type of reactor (CSTR, PFR, RR, or network)**

* **Verify through simulation**

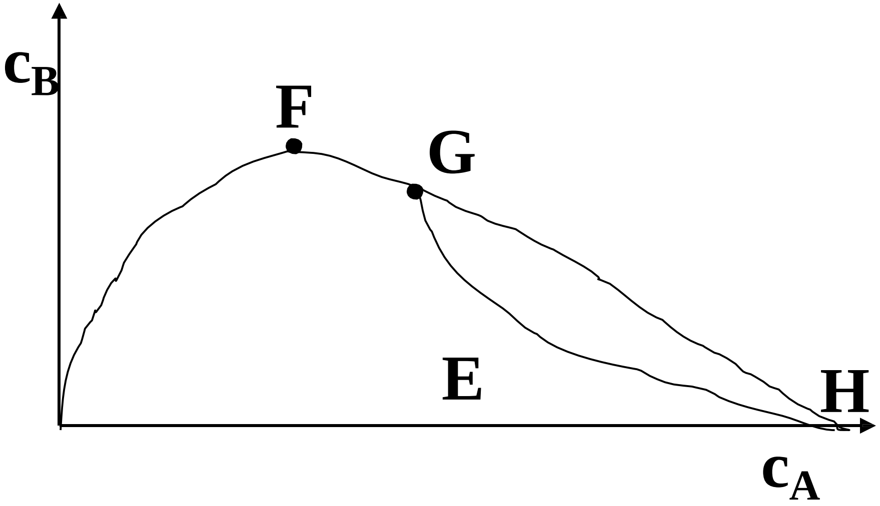
Basic Steps in Reactor Design & Analysis

* **What happens when there are multiple reactions?**

A = B = C **series** $dc_A/d\tau = r_A$ $dc_B/d\tau = r_B$

or, **A + B = C; 2A = D parallel**

Concept of Attainable region helps to select the reactors and the optimal conversion at the highest selectivity



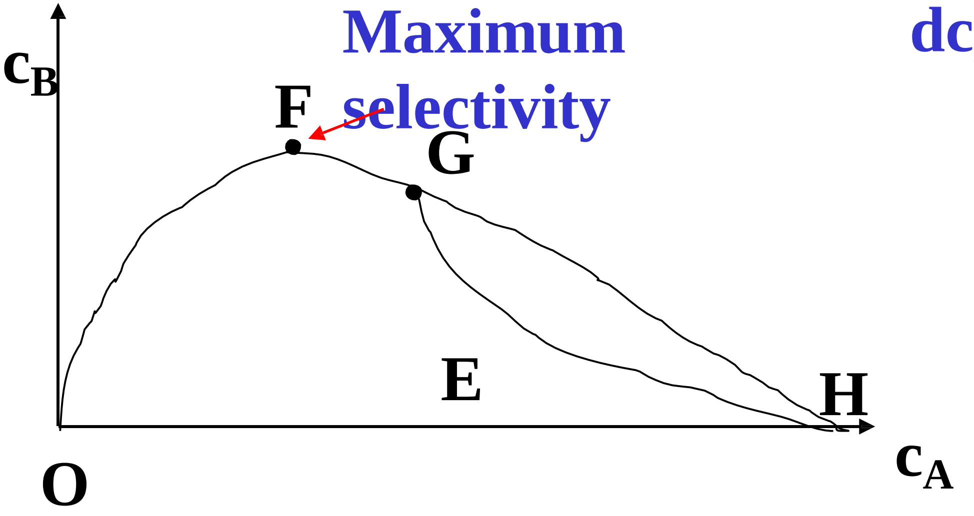
$dc_B/dc_A = r_B/r_A$ **for PFR**

$(c_B-c_{B0})/(c_A-c_{A0}) = r_B/r_A$ **for CSTR**

For known r_A & r_B, solve for c_B at different values of c_A to obtain the plot of c_B vs c_A

Basic Steps in Reactor Design & Analysis – Multiple Reactions

Concept of Attainable region helps to select the reactors and the optimal conversion at the highest selectivity



Maximum selectivity

$dc_A/d\tau = r_A$ $dc_B/d\tau = r_B$

$dc_B/dc_A = r_B/r_A$ for PFR

$(c_B-c_{B0})/(c_A-c_{A0}) = r_B/r_A$ for CSTR

For known r_A & r_B, solve for c_B at different values of c_A to obtain the plot of c_B vs c_A

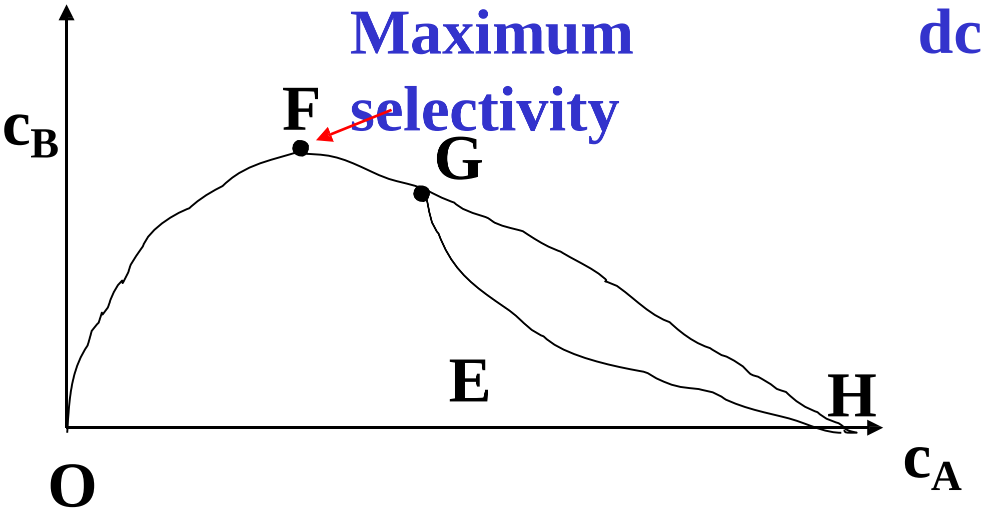
Convex region OFGH

Non-convex region OFGEH

Reactor with non-convex attainable region does not achieve the reaction that is possible or attainable

Basic Steps in Reactor Design & Analysis – Multiple Reactions

Concept of Attainable region helps to select the reactors and the optimal conversion at the highest selectivity



Maximum selectivity

$dc_A/d\tau = r_A$ $dc_B/d\tau = r_B$

$dc_B/dc_A = r_B/r_A$ for PFR

$(c_B - c_{B0})/(c_A - c_{A0}) = r_B/r_A$ for CSTR

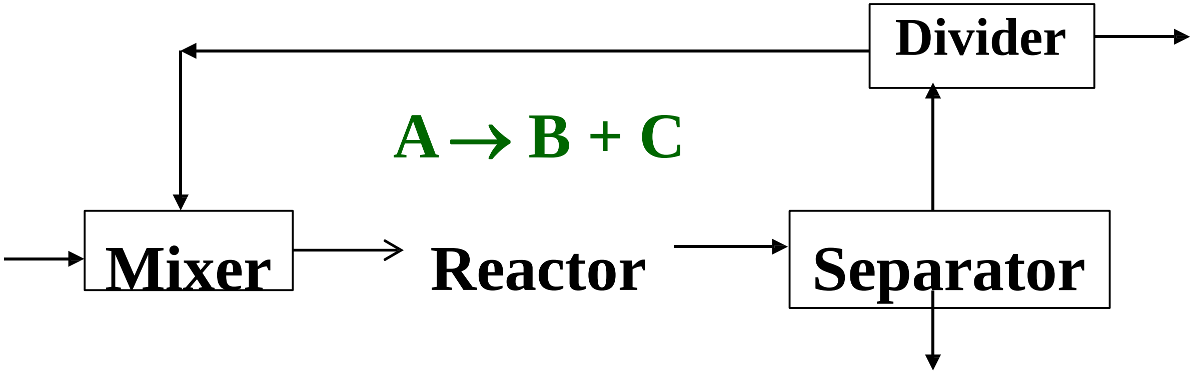
For known r_A & r_B, solve for c_B at different values of c_A to obtain the plot of c_B vs c_A

Convex region OFGH

Non-convex region OFGEH

Reactor with non-convex attainable region (AR) does not achieve the reaction that is possible or attainable – Maximum AR must be convex, reaction vectors cannot point outward from the boundary

Design-Analysis Issues with Reactor-Separation-Recycle Systems



Divider

$A \rightarrow B + C$

Mixer

Reactor

Separator

Assume perfect separation of A from B and C

Conversion of reactants directly related to recycle flow as well as design and operation of the reactor

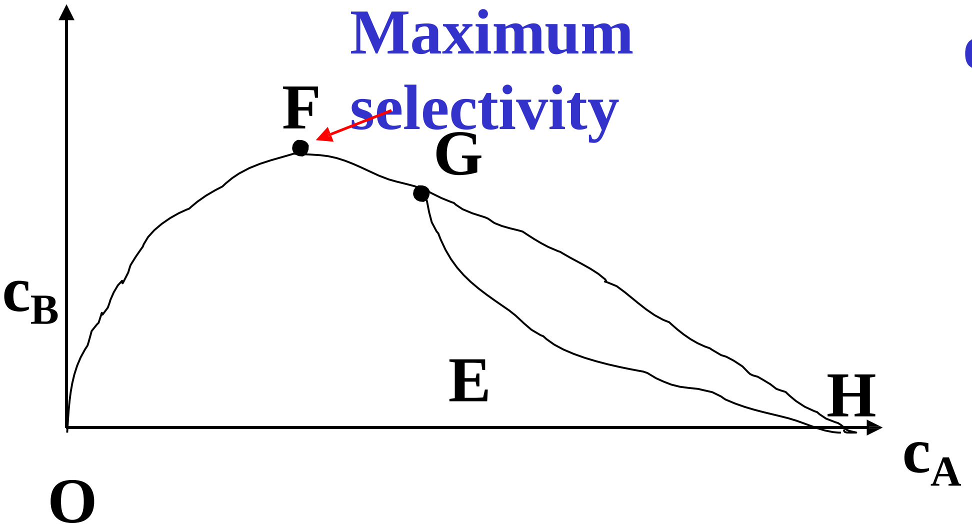
$D_a – X_A/(1- X_A)[1 - \alpha(1 – X_A)] = 0$

Where, $D_a = kV\rho/F_A \geq 1$

X_A = conversion of A = (amount of A reacted) / (amount of A entering the reactor)

α is separation factor of A in the separator

Exercise 13.1: Analysis with AR-concept



$dc_A/d\tau = r_A$ $dc_B/d\tau = r_B$

$dc_B/dc_A = r_B/r_A$ for PFR

$(c_B\text{-}c_{B0})/(c_A\text{-}c_{A0}) = r_B/r_A$ for CSTR

For known r_A & r_B, solve for c_B at different values of c_A to obtain the plot of c_B vs c_A

Consider the following reaction scheme

$$A \leftrightarrow B \rightarrow C \text{ and } 2A \rightarrow D$$

$$k_{1f} = 0.01;\ k_{1r} = 5;\ k_2 = 10,\ k_3 = 100$$

$$r_A = -k_{1f}c_A + k_{1r}c_B - k_3(c_A)^2 \quad ;\ r_B = k_{1f}c_A - k_{1r}c_B - k_2c_B$$

Find the reactor composition c_A where the selectivity of B is the highest with a PFR and a CSTR. Then check the residence time – temperature that gives a selectivity as close as possible to the highest. Then work out the remaining design variables

Introduction to Mass Integration

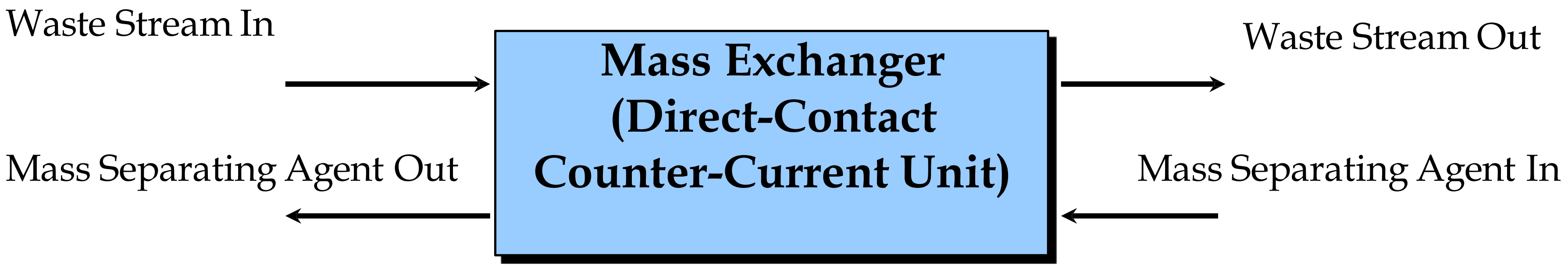
Book of Robin Smith & notes of Dr. R. Dunn – Consultant, USA (Mass Integration)

- ***Robin Smith, Chemical Process Design & Integration, Wiley, England, 2005***

- ***El-Halwagi and Manousiouthakis. (1989, 1990)***
- ***El-Halwagi and Srinivas (1992)***
- ***Srinivas and El-Halwagi (1994a)***
- ***Dunn and El-Halwagi (1996)***

End-of-the-Pipe Design Tools

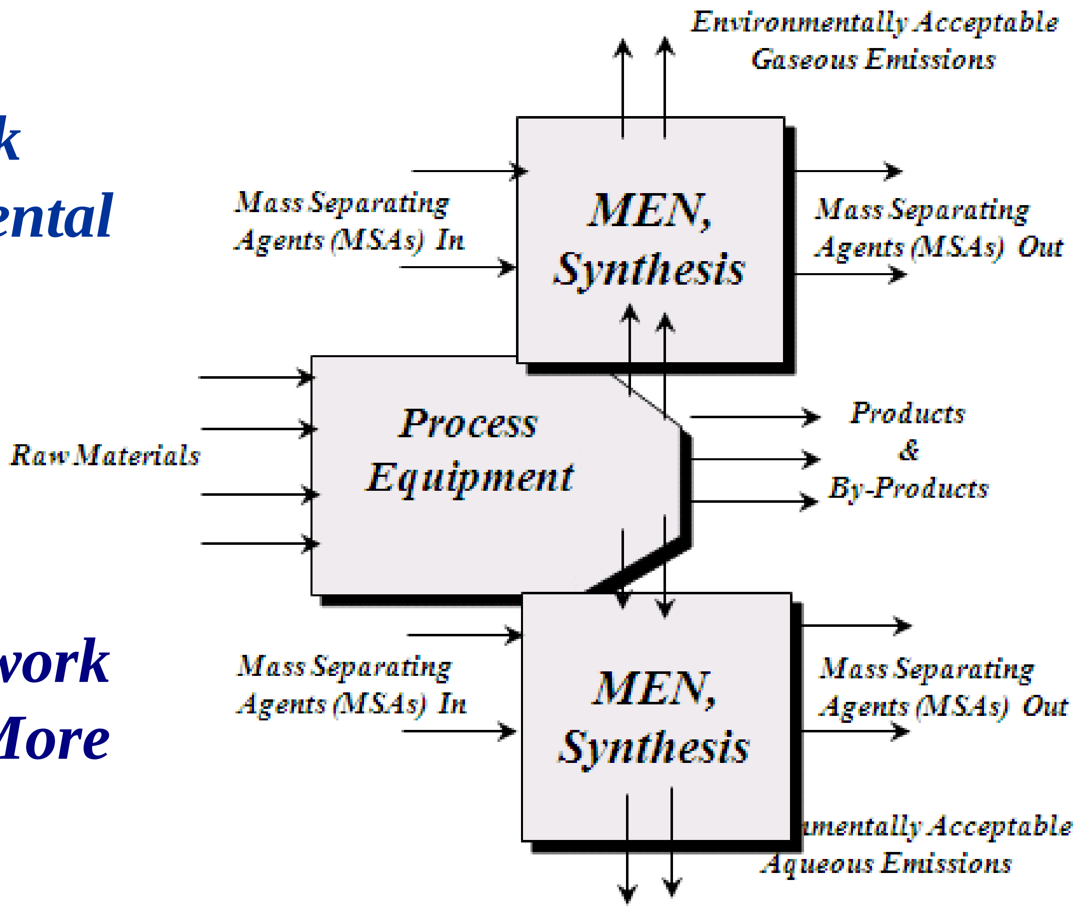
Schematic of a Single Mass-Exchanger for Environmental Process Design



Examples of Mass-Exchangers are Absorbers, Adsorbers, Ion-Exchange Units, Liquid-Liquid Extraction Units, etc.

End-of-the-Pipe Design Tools

Mass-Exchange Network Synthesis for Environmental Process Design

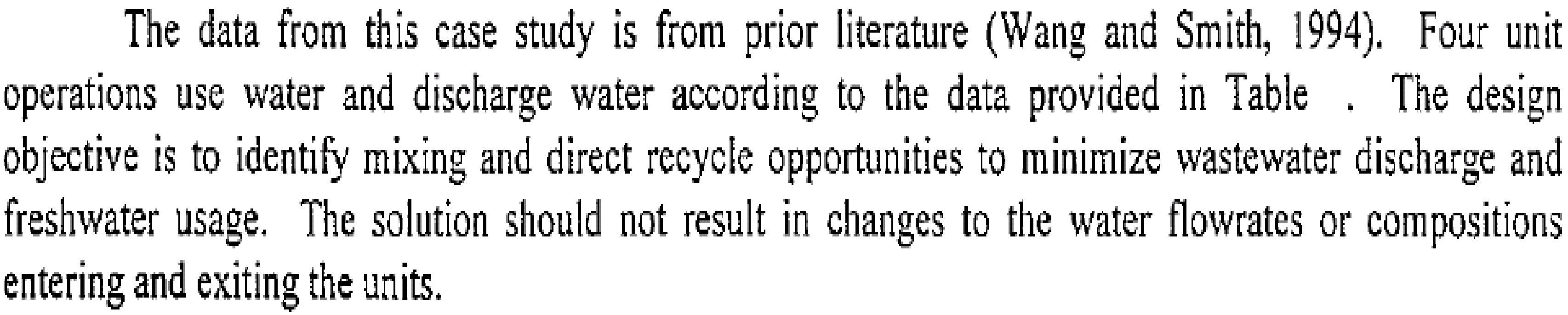


A Mass Exchange Network is a System of One or More Mass Exchangers

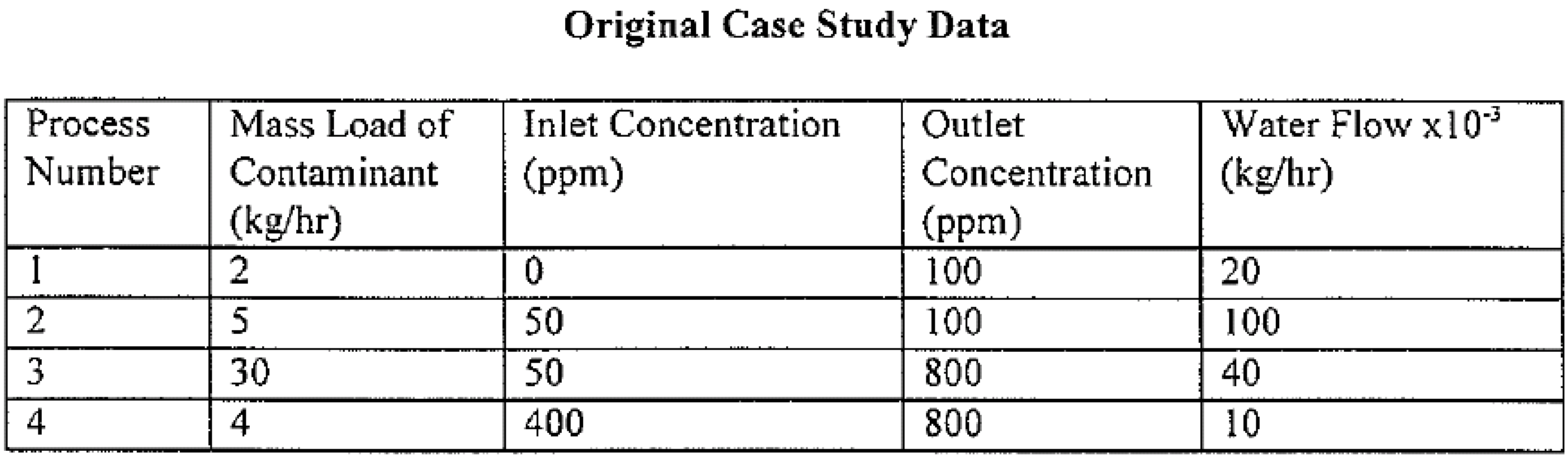
Mass Exchange Network (MEN) Solution Strategies

- Graphical Techniques
- Targeting Approach
  - LP to Minimize Operating Cost
  - MILP to Minimize the Number of Units

Minimum fresh-water & water reuse



The data from this case study is from prior literature (Wang and Smith, 1994). Four unit operations use water and discharge water according to the data provided in Table . The design objective is to identify mixing and direct recycle opportunities to minimize wastewater discharge and freshwater usage. The solution should not result in changes to the water flowrates or compositions entering and exiting the units.



Original Case Study Data

Process Number	Mass Load of Contaminant (kg/hr)	Inlet Concentration (ppm)	Outlet Concentration (ppm)	Water Flow x10^{-3} (kg/hr)
1	2	0	100	20
2	5	50	100	100
3	30	50	800	40
4	4	400	800	10

Step 1: Create the source & sink tables

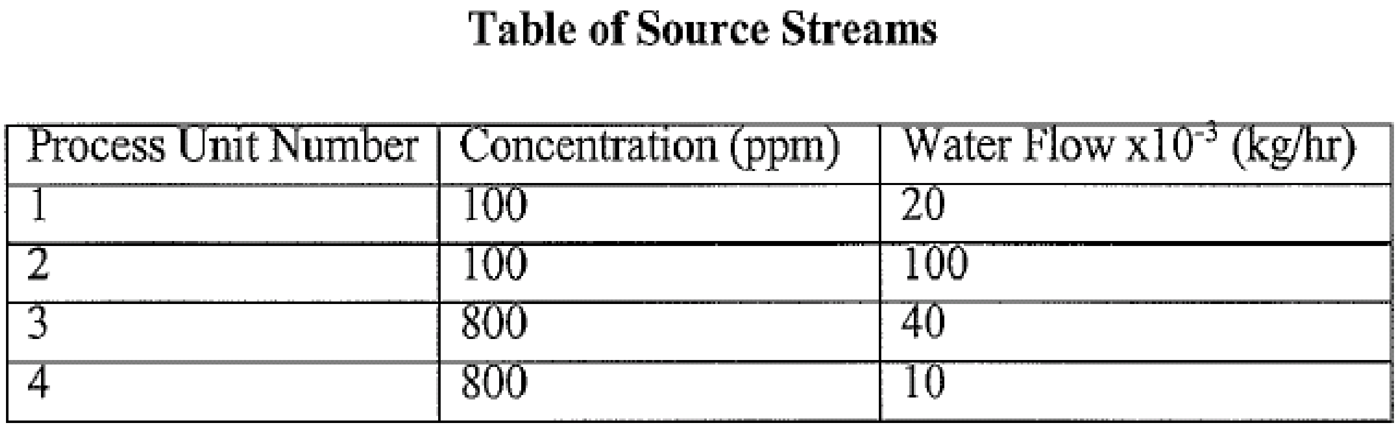


Table of Source Streams

Process Unit Number	Concentration (ppm)	Water Flow x10^{-3} (kg/hr)
1	100	20
2	100	100
3	800	40
4	800	10

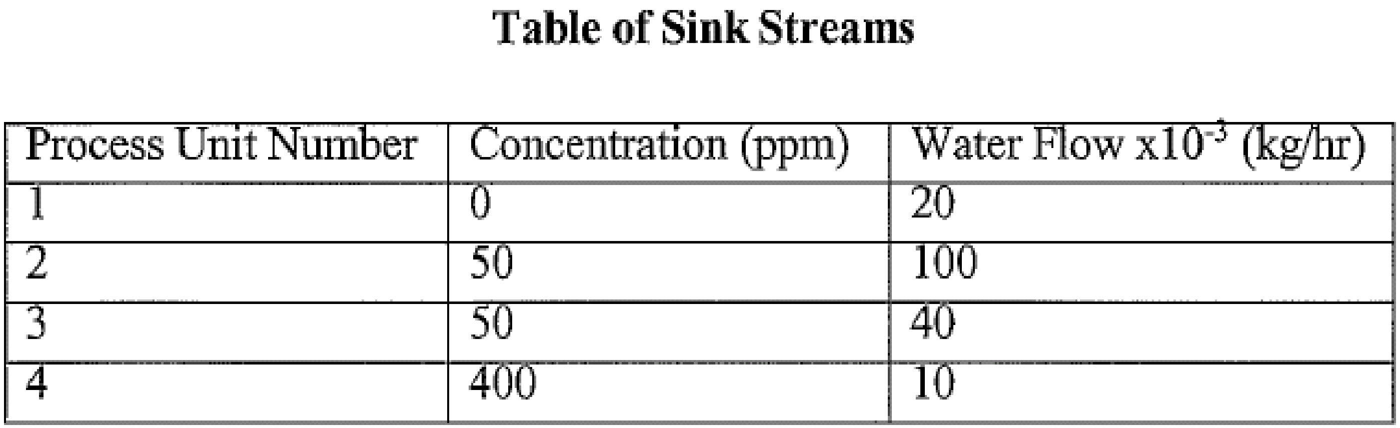
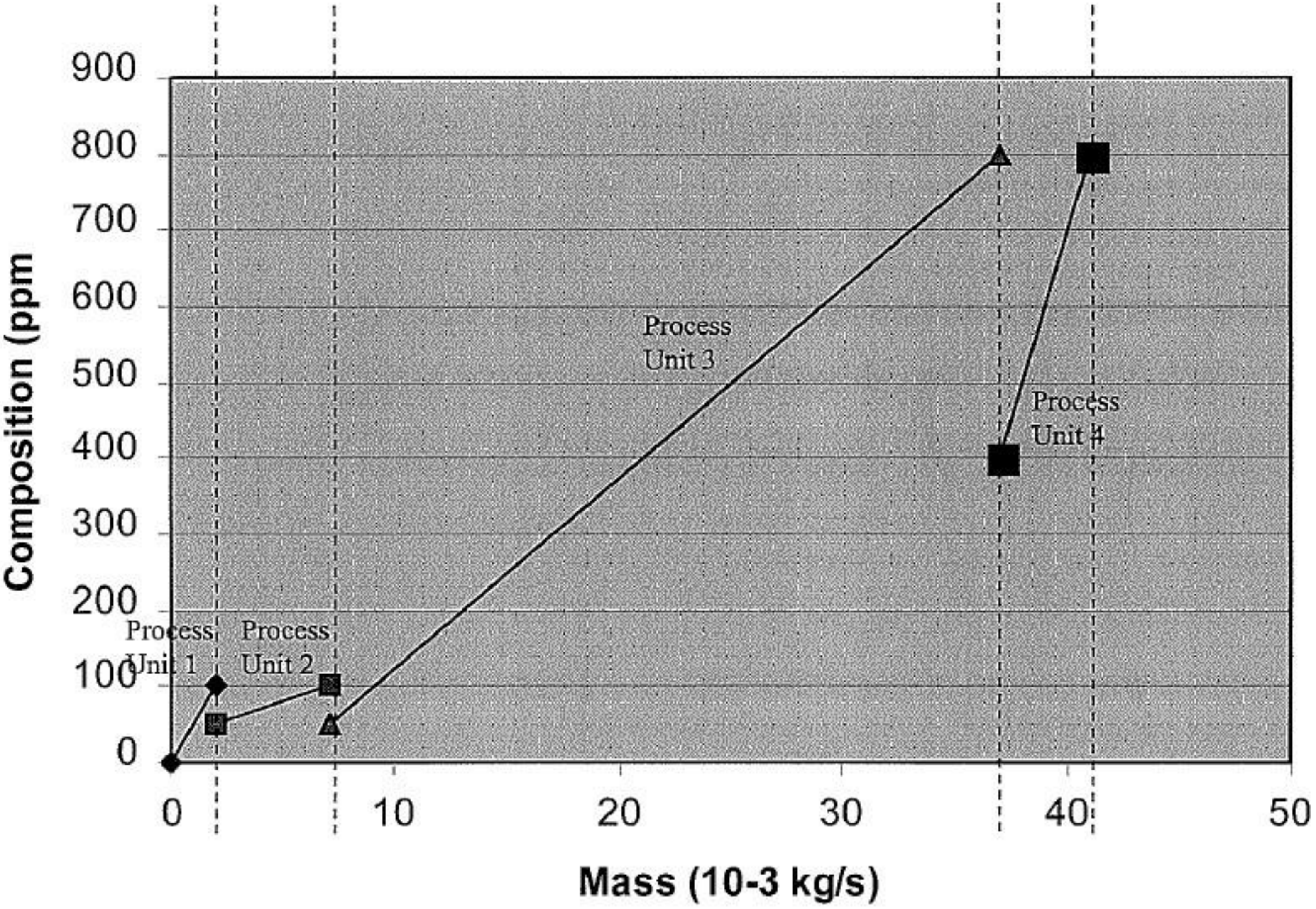


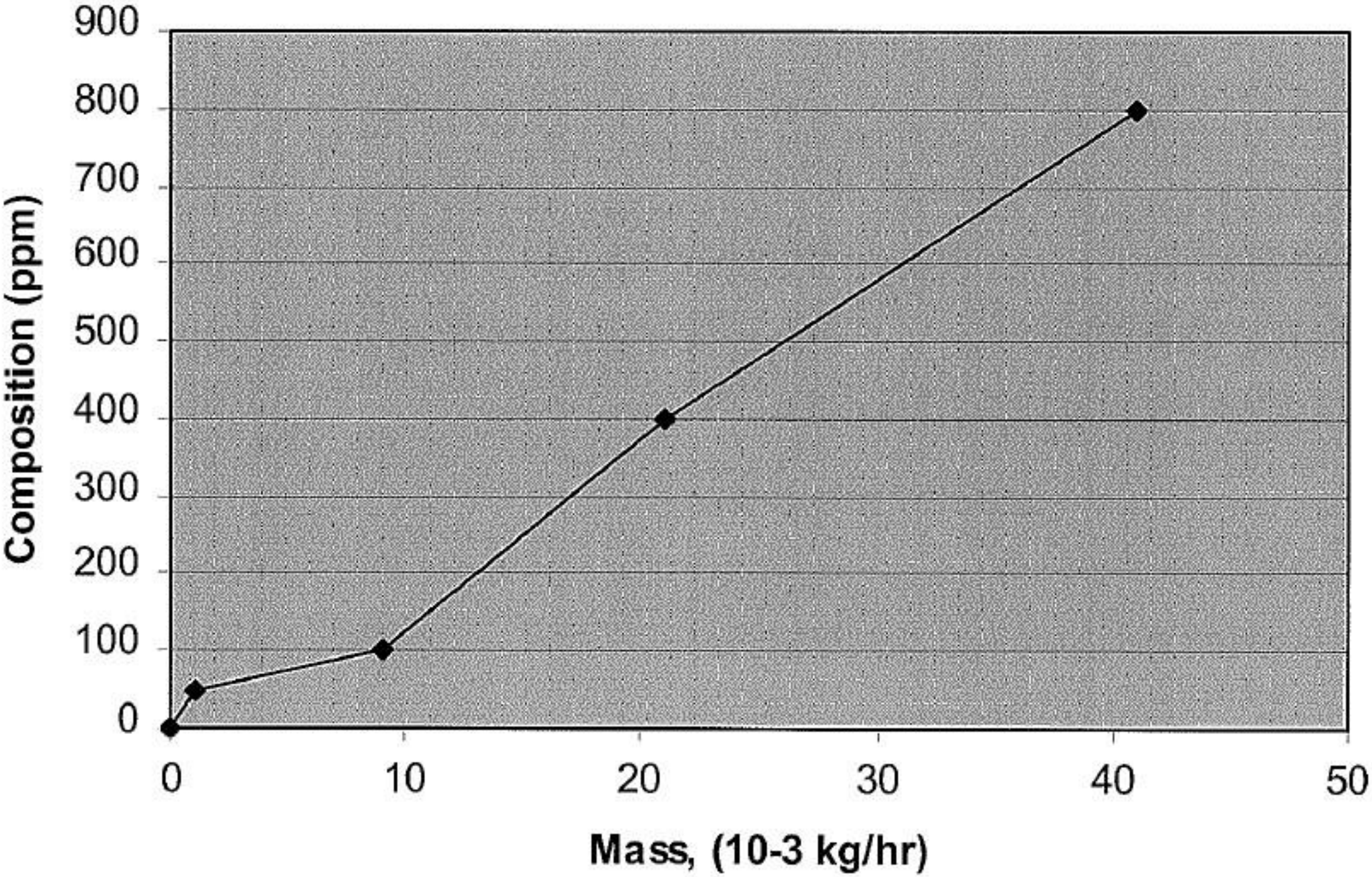
Table of Sink Streams

Process Unit Number	Concentration (ppm)	Water Flow x10^{-3} (kg/hr)
1	0	20
2	50	100
3	50	40
4	400	10

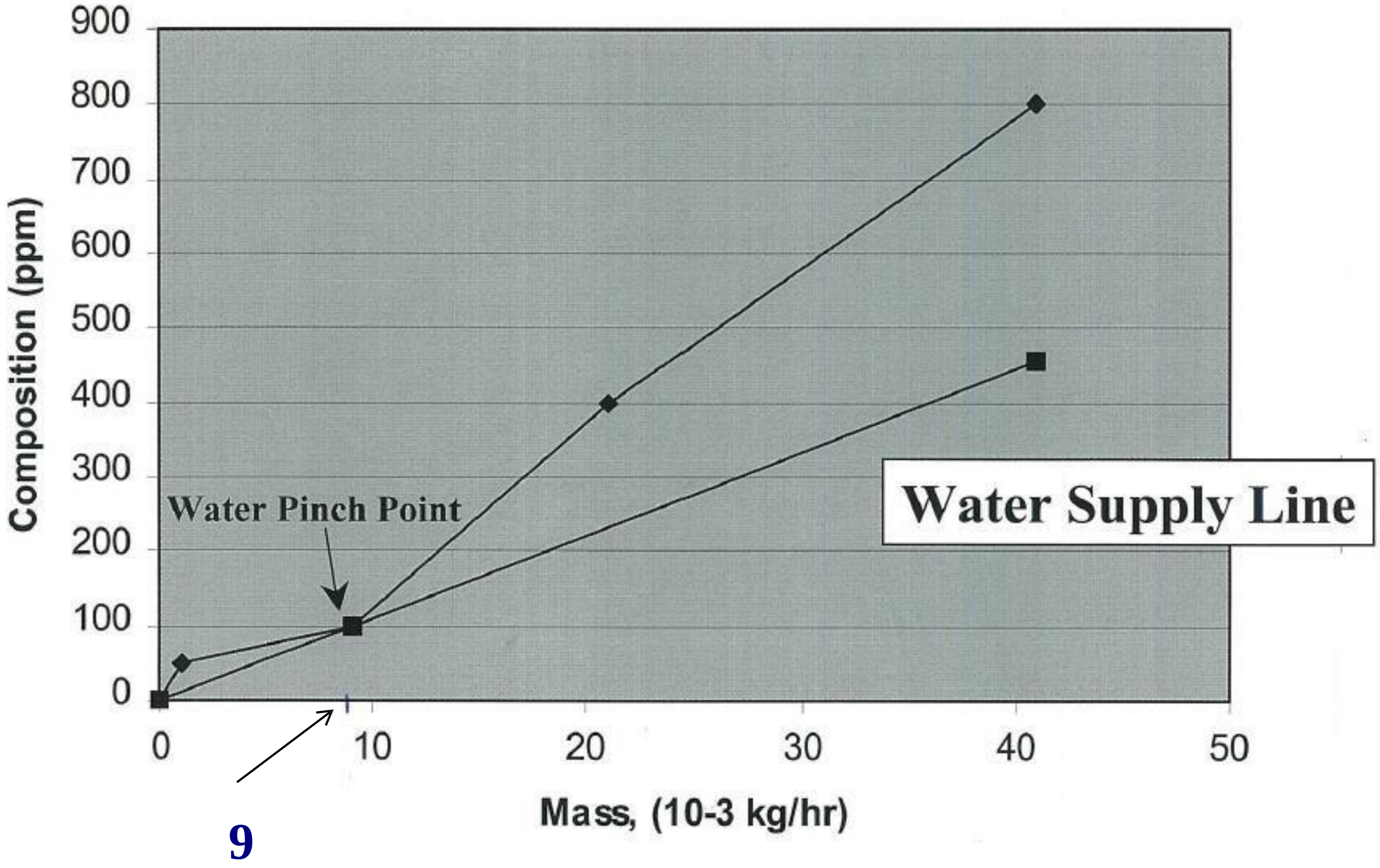
Step 2: Draw Limiting Water Profiles



Step 3: Draw Limiting Composite Curve

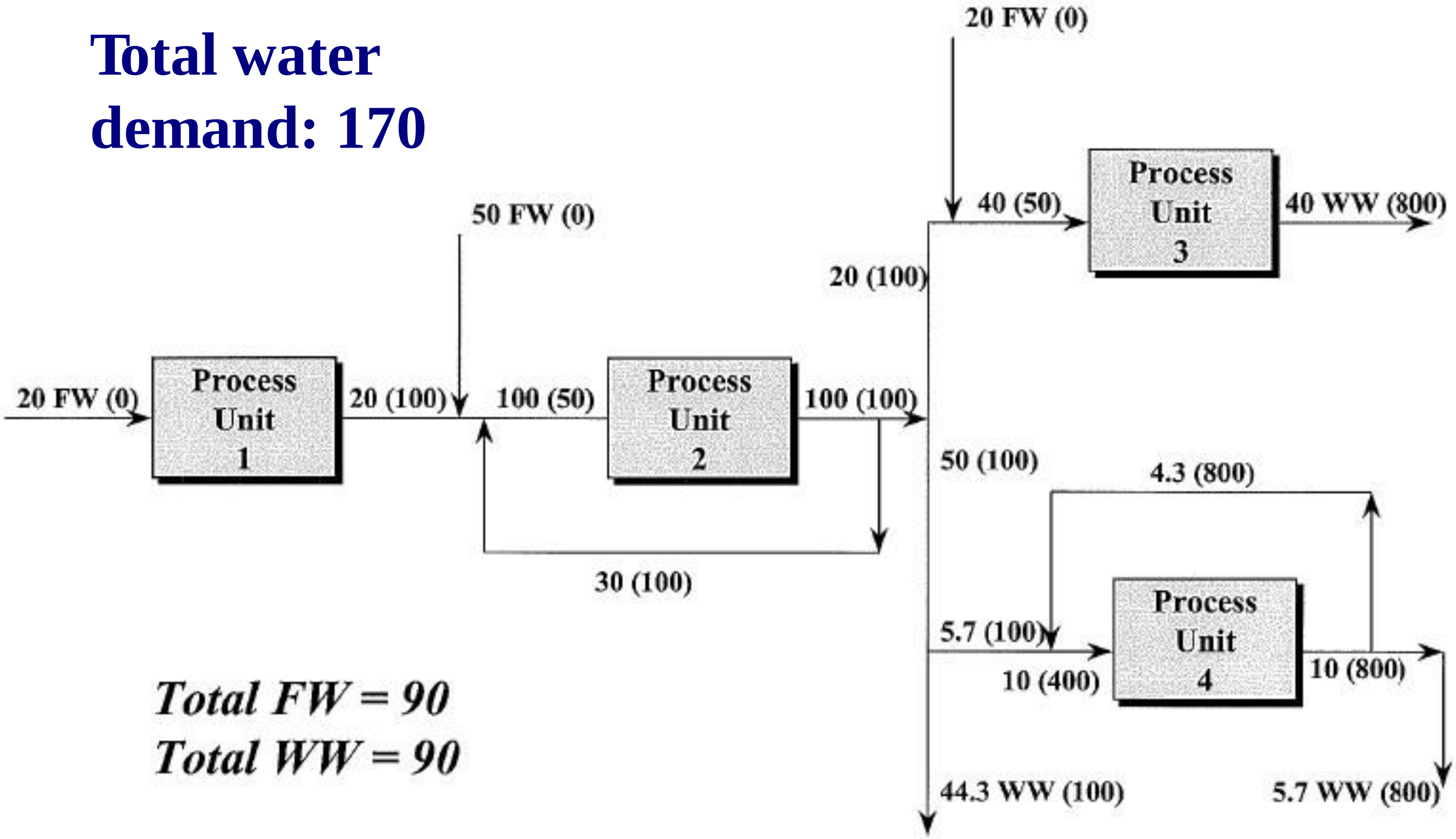


Step 4: Draw Water Pinch Diagram



The Network:

Total water demand: 170



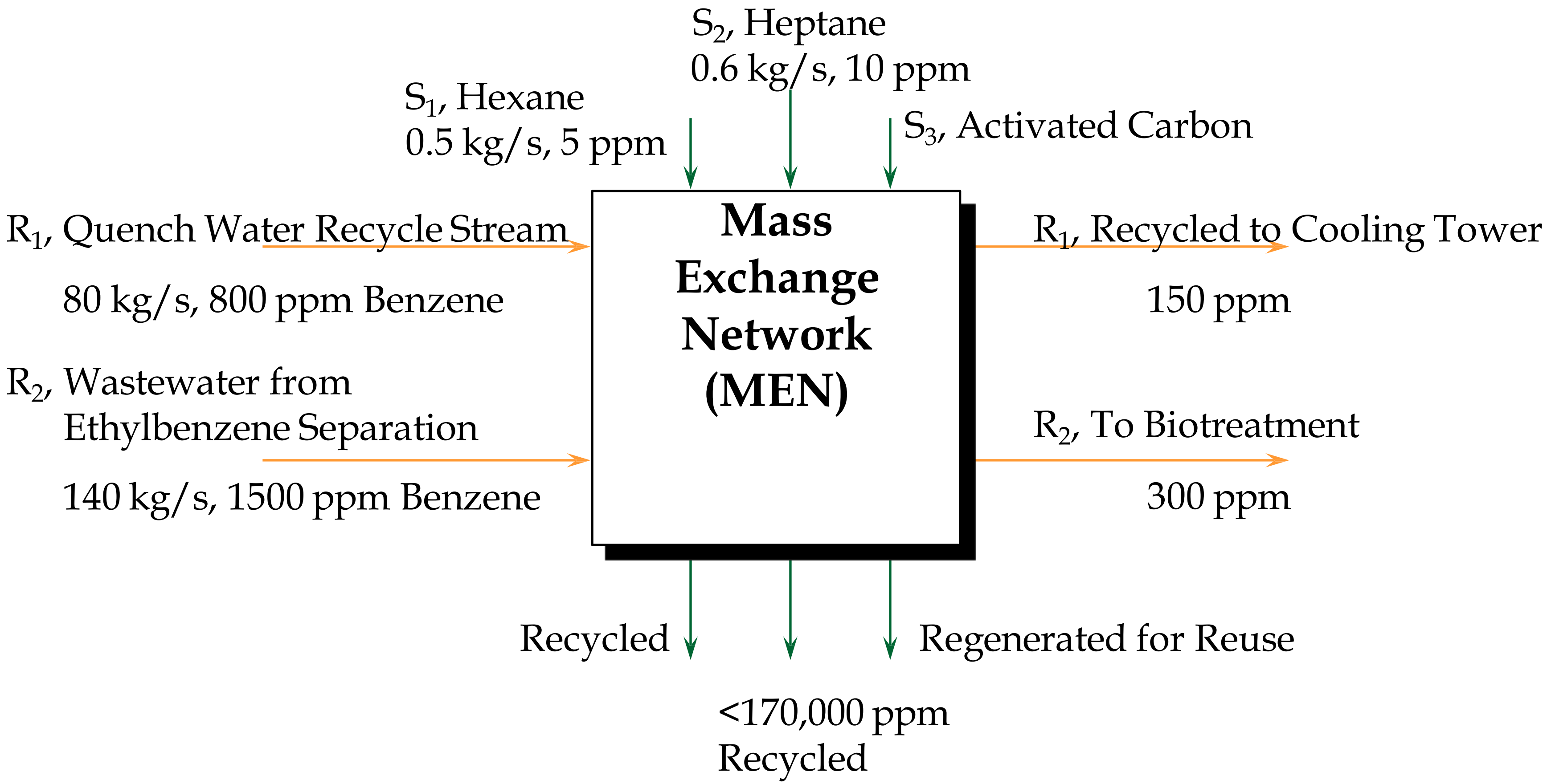
Total FW = 90
Total WW = 90

Water reuse: 80

FW = Fresh Water Usage
WW = Wastewater Discharge
Concentrations in brackets

Another MEN Example *(Dunn and El-Halwagi, 1996)*

Consider the following solvent recovery task for an ethylene/ethylbenzene plant



S_2, Heptane
0.6 kg/s, 10 ppm

S_1, Hexane
0.5 kg/s, 5 ppm

S_3, Activated Carbon

R_1, Quench Water Recycle Stream
80 kg/s, 800 ppm Benzene

R_2, Wastewater from Ethylbenzene Separation
140 kg/s, 1500 ppm Benzene

Mass Exchange Network (MEN)

R_1, Recycled to Cooling Tower
150 ppm

R_2, To Biotreatment
300 ppm

Recycled

<170,000 ppm
Recycled

Regenerated for Reuse

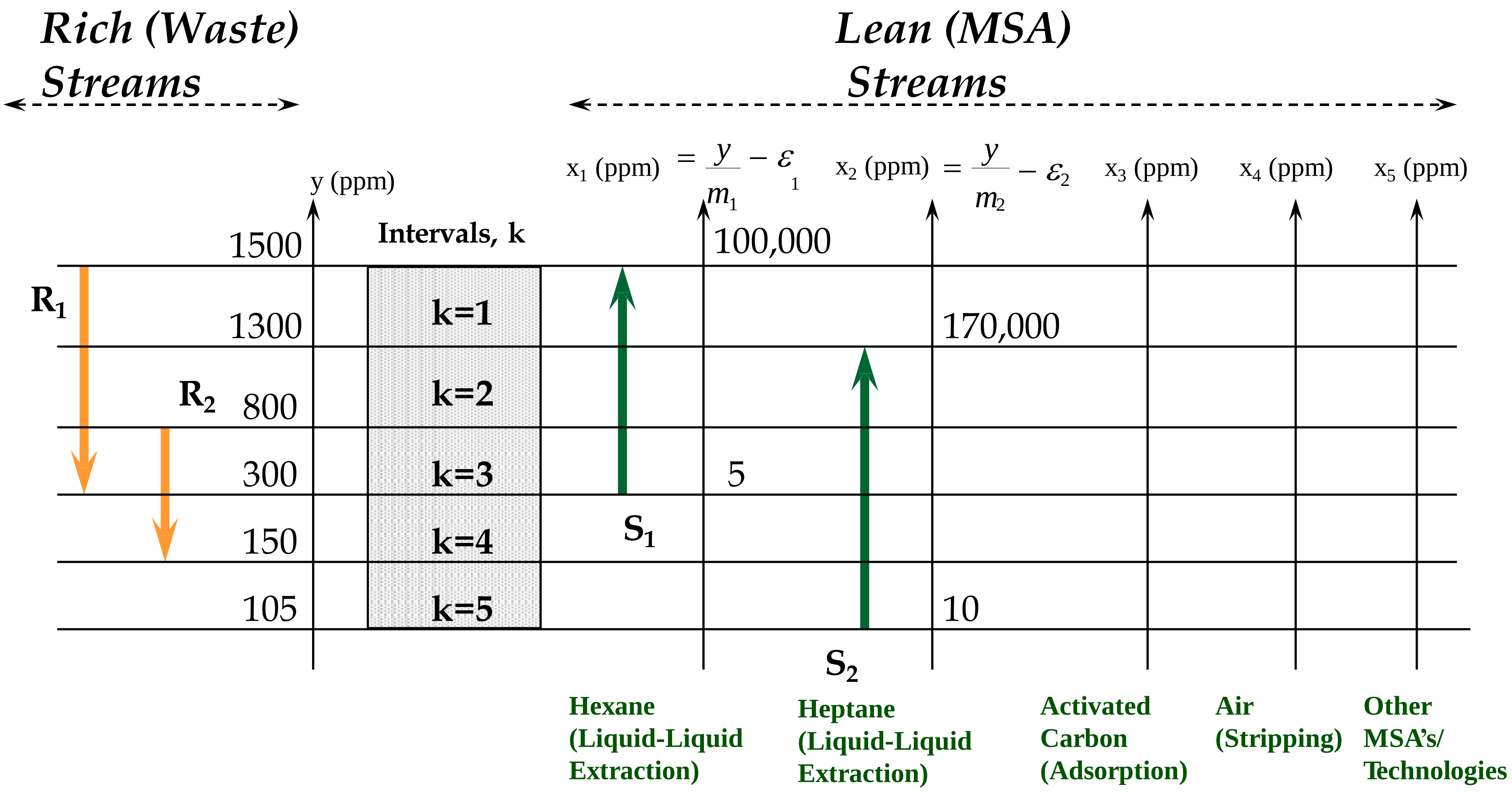
Data for the Wastewater Streams of an Ethylbenzene Plant

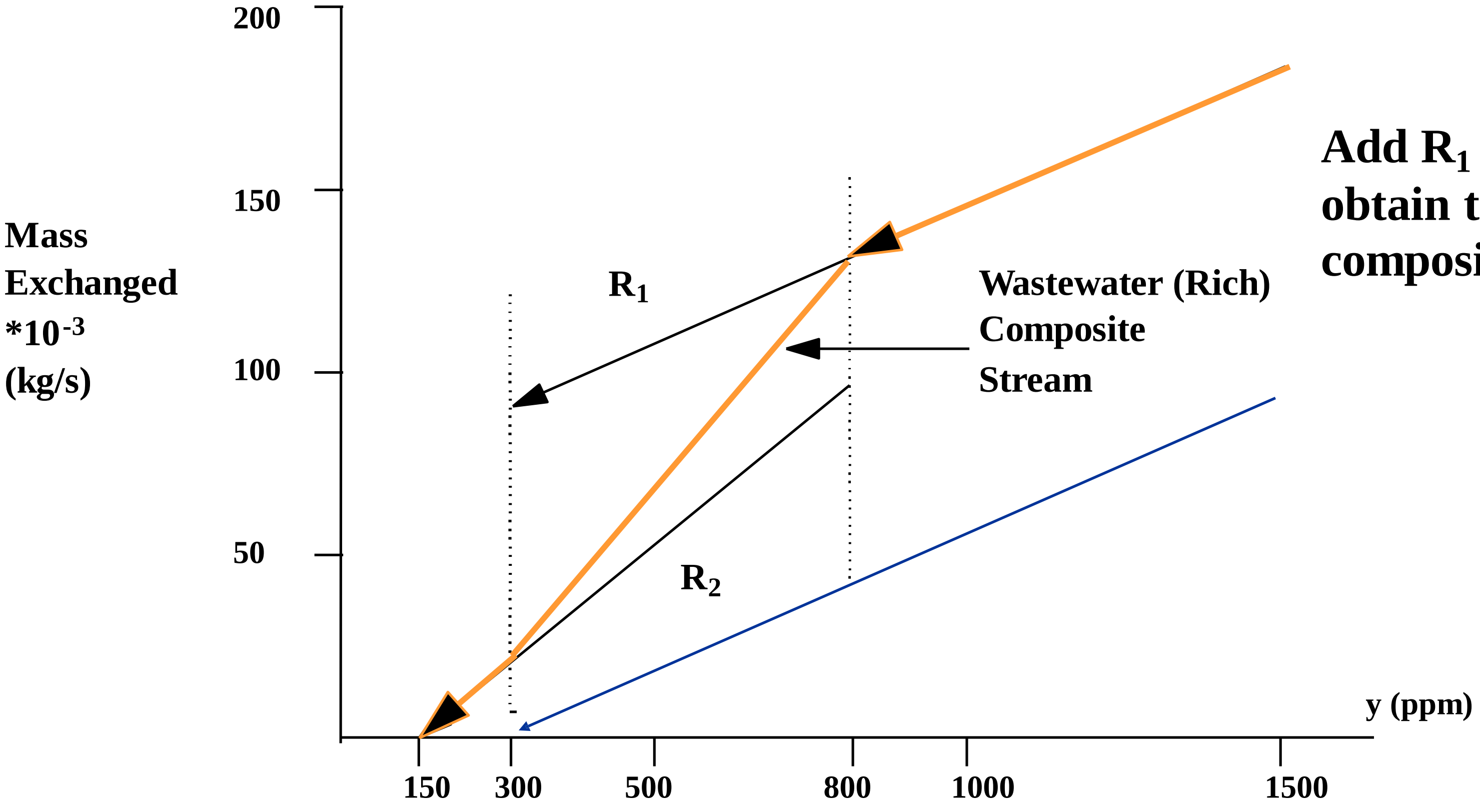
Stream	Description	Flowrate (kg/s)	Supply Composition (ppm)	Target Composition (ppm)	Stream Disposition
R_2	Wastewater from Settling	140	800	150	Recycled to Cooling Tower
R_1	Wastewater from Ethylbenzene Separation	80	1500	300	Biotreatment

Data for the Process MSA's Available for the Benzene Separation Task

Stream	Description	Flowrate (kg/s)	Supply Composition (ppm)	Maximum Target Composition (ppm)	Minimum Mass Transfer Driving Force (ppm)
S_1	Hexane	0.5	5	-	25,000
S_2	Heptane	0.6	10	170,000	15,000

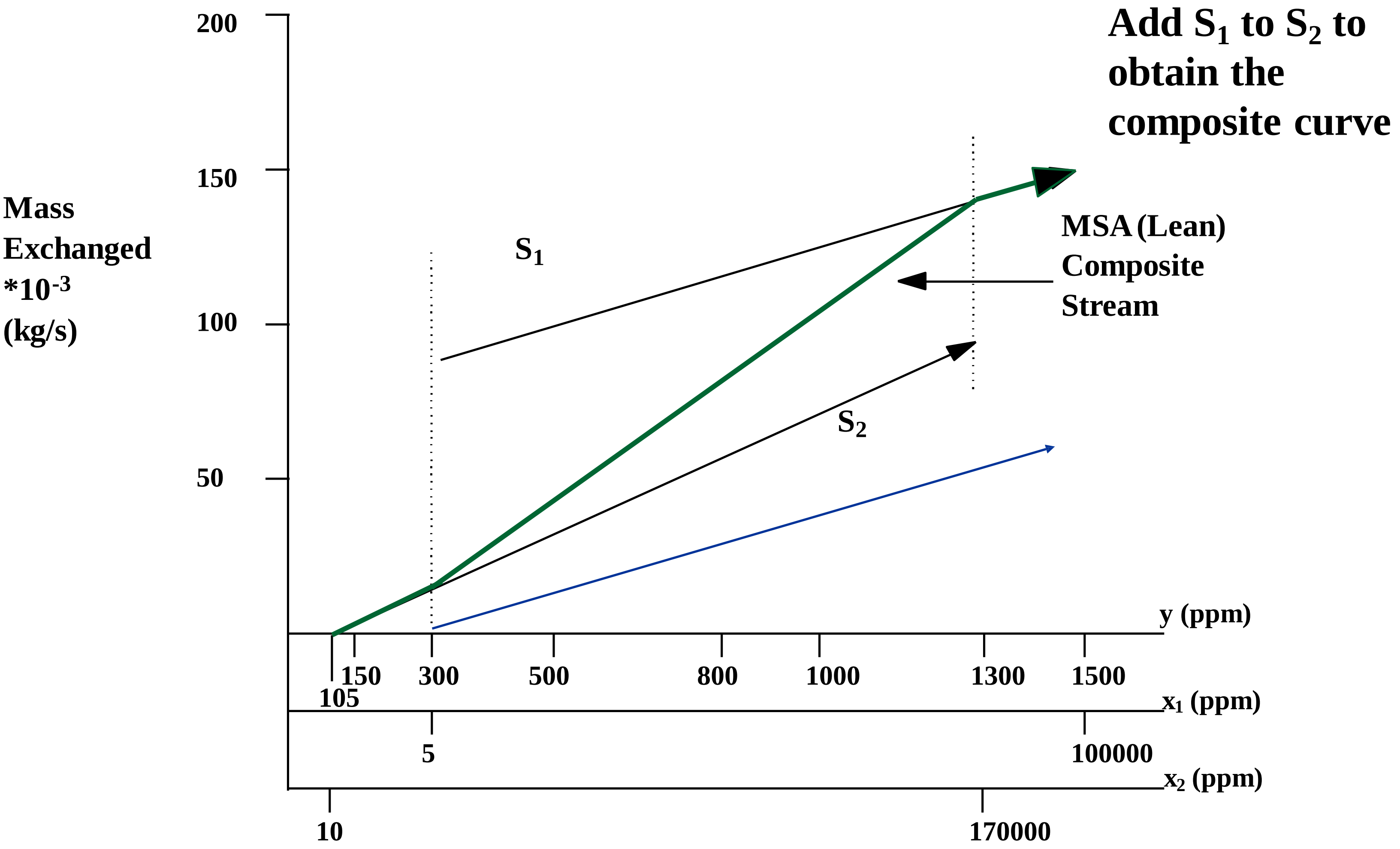
Composition-Interval-Diagram (CID) for the Benzene Recovery Example





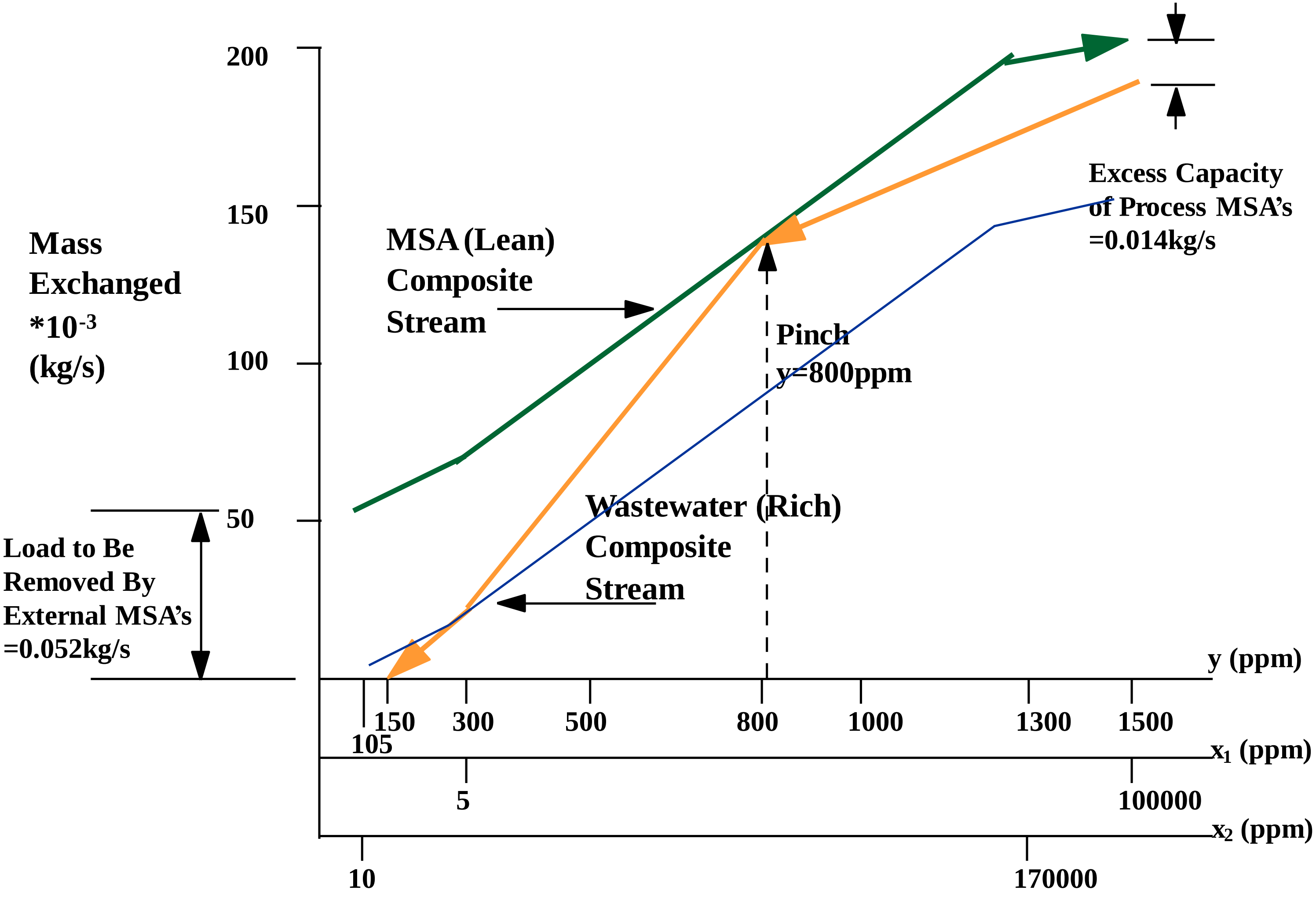
Add R_1 to R_2 to obtain the composite curve

Construction of the Wastewater Composite Stream on The Mass Exchange Pinch Diagram



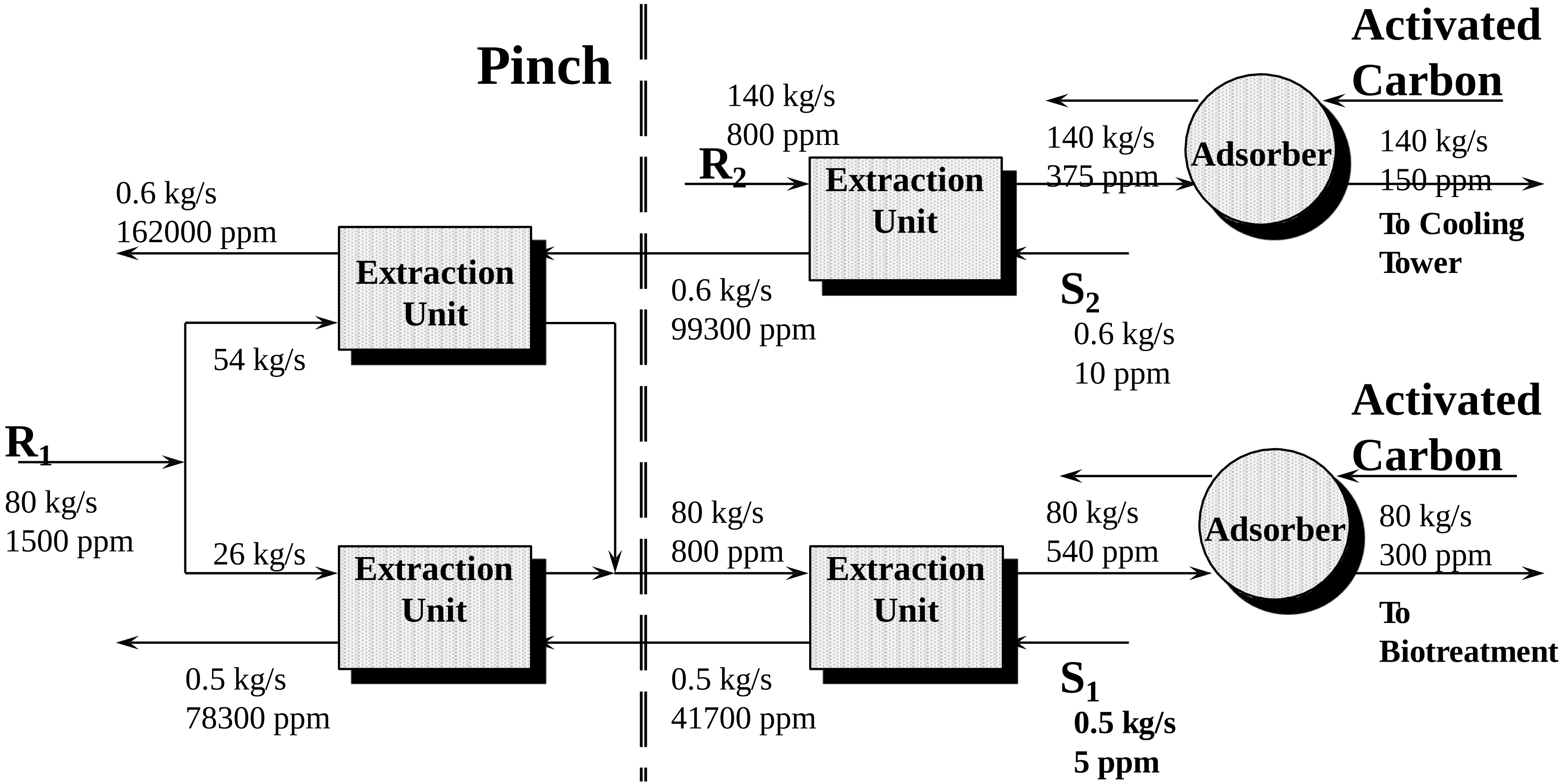
Add S_1 to S_2 to obtain the composite curve

Construction of the MSA Composite Stream on The Mass Exchange Pinch Diagram



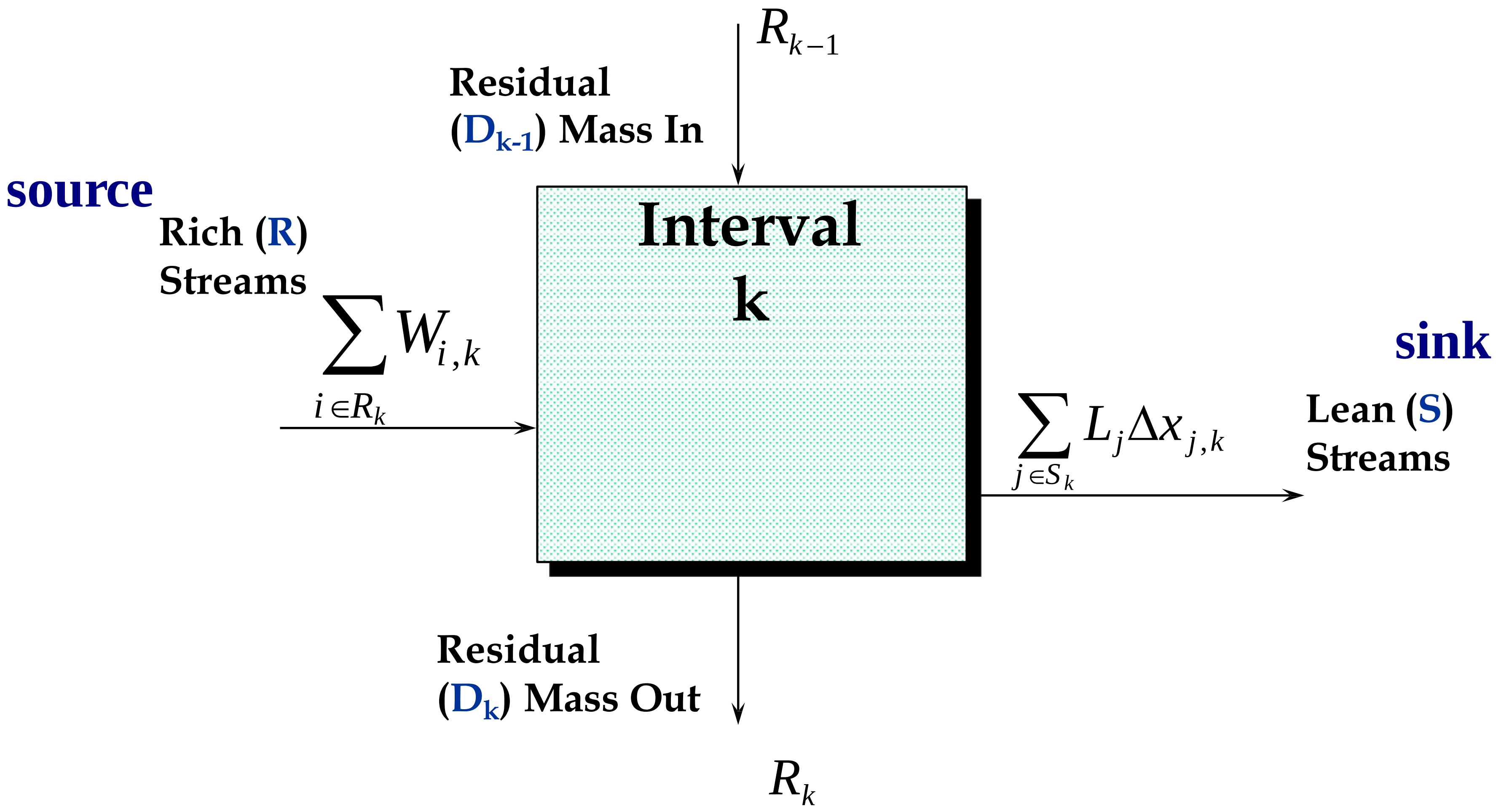
The Mass Exchange Pinch Diagram for the Benzene Separation Case Study

Mass Exchange Network Configuration for the Illustrative Example



Targeting Approach

Mass Balance for an Interval k



R_{k-1}

Residual
(D_{k-1}) Mass In

source

Rich (R)
Streams

$$\sum_{i \in R_k} W_{i,k}$$

Interval
k

sink

$$\sum_{j \in S_k} L_j \Delta x_{j,k}$$

Lean (S)
Streams

Residual
(D_k) Mass Out

R_k

Linear Program (LP) to Minimize Operating Cost

Operating Cost Objective Function

$$\textit{minimize cost } (C) = \sum_{j \in S} c_j L_j$$

Interval Overall Mass Balances

Subject to:

$$R_k - R_{k-1} - \sum_{m \in S_k} L_j \Delta x_{j,k} = \sum_{i \in H_k} W_{i,k}^R \qquad k = 1, 2., \ldots, K$$

Non-negative Stream Flowrates

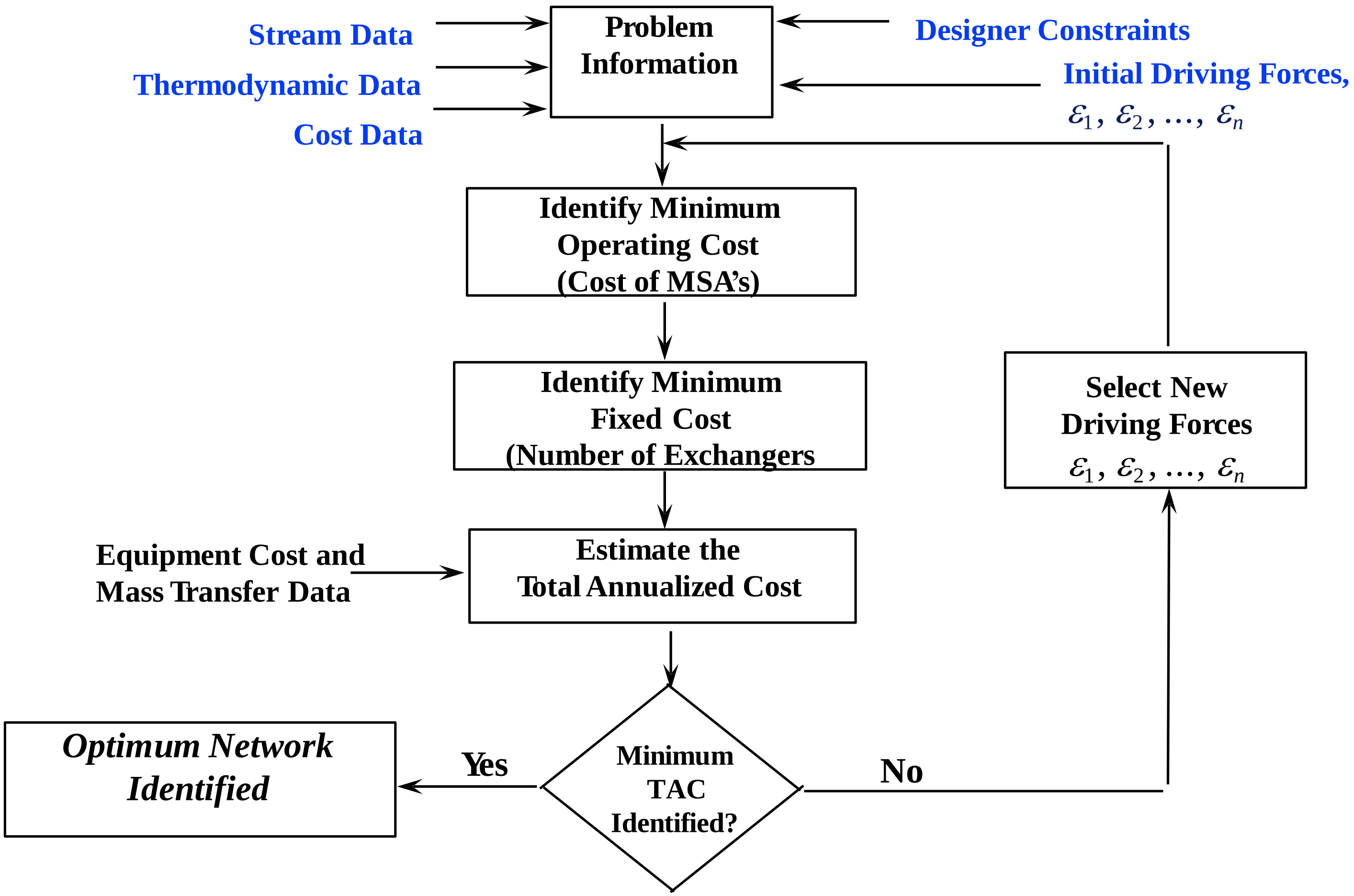
$$L_j \geq 0 \qquad j \in S$$

Residual Constraints

$$R_0 = R_K = 0$$

$$R_k \geq 0 \qquad k = 1, 2, \ldots, K-1$$

Schematic Flowsheet to Synthesize Optimal MEN’s



Stream Data

Thermodynamic Data

Cost Data

Problem Information

Designer Constraints

Initial Driving Forces, $\varepsilon_1, \varepsilon_2, \ldots, \varepsilon_n$

Identify Minimum Operating Cost (Cost of MSA’s)

Identify Minimum Fixed Cost (Number of Exchangers

Equipment Cost and Mass Transfer Data

Estimate the Total Annualized Cost

Minimum TAC Identified?

Yes

Optimum Network Identified

No

Select New Driving Forces $\varepsilon_1, \varepsilon_2, \ldots, \varepsilon_n$

Identifying the Minimum Total Annualized Cost for a Mass Exchange Network