Modeling and Optimization of Biorefineries

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Motivation

- **Motivation for Integrated Biorefineries**
  - Today's energy and chemical industries are fossil fuel based, therefore unsustainable and contributing to environmental deterioration and economic and political vulnerability.
  - The integrated biorefinery has the opportunity to provide a strong, self-dependent, sustainable alternative for the production of chemicals and fuels.
  - One resource that is readily available is our forest-based biomass, which is particularly concentrated in the Southeastern United States.

Background

- **Benefits of Integrated Biorefineries**
  - Economic sustainability through renewable feedstocks
  - Increased biomass utilization
  - CO_2 neutral power and chemical production

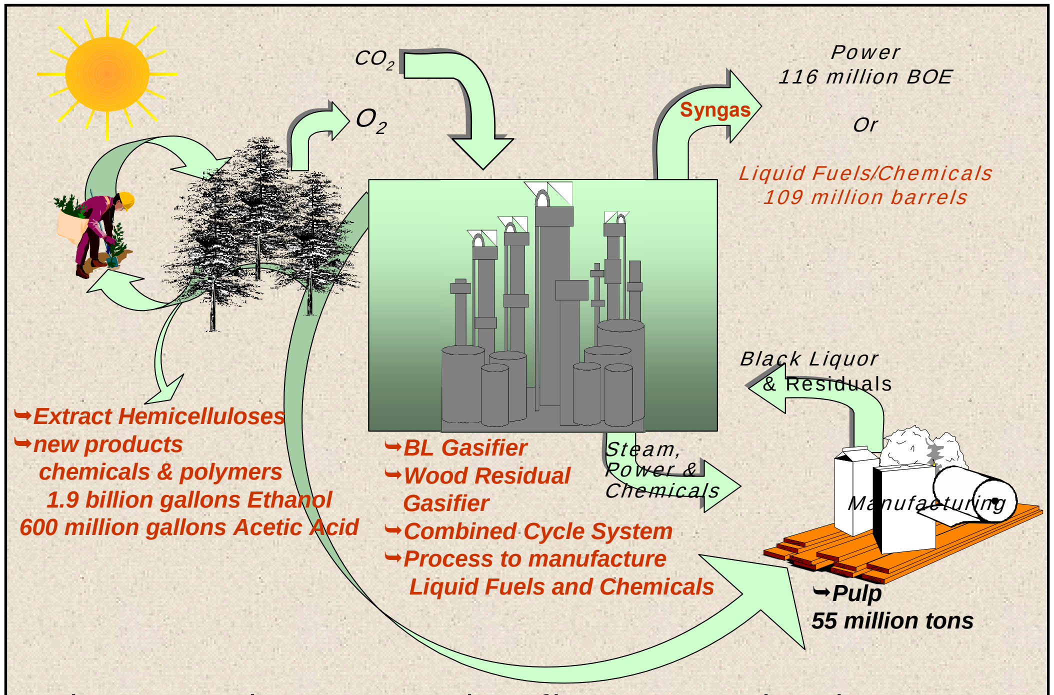
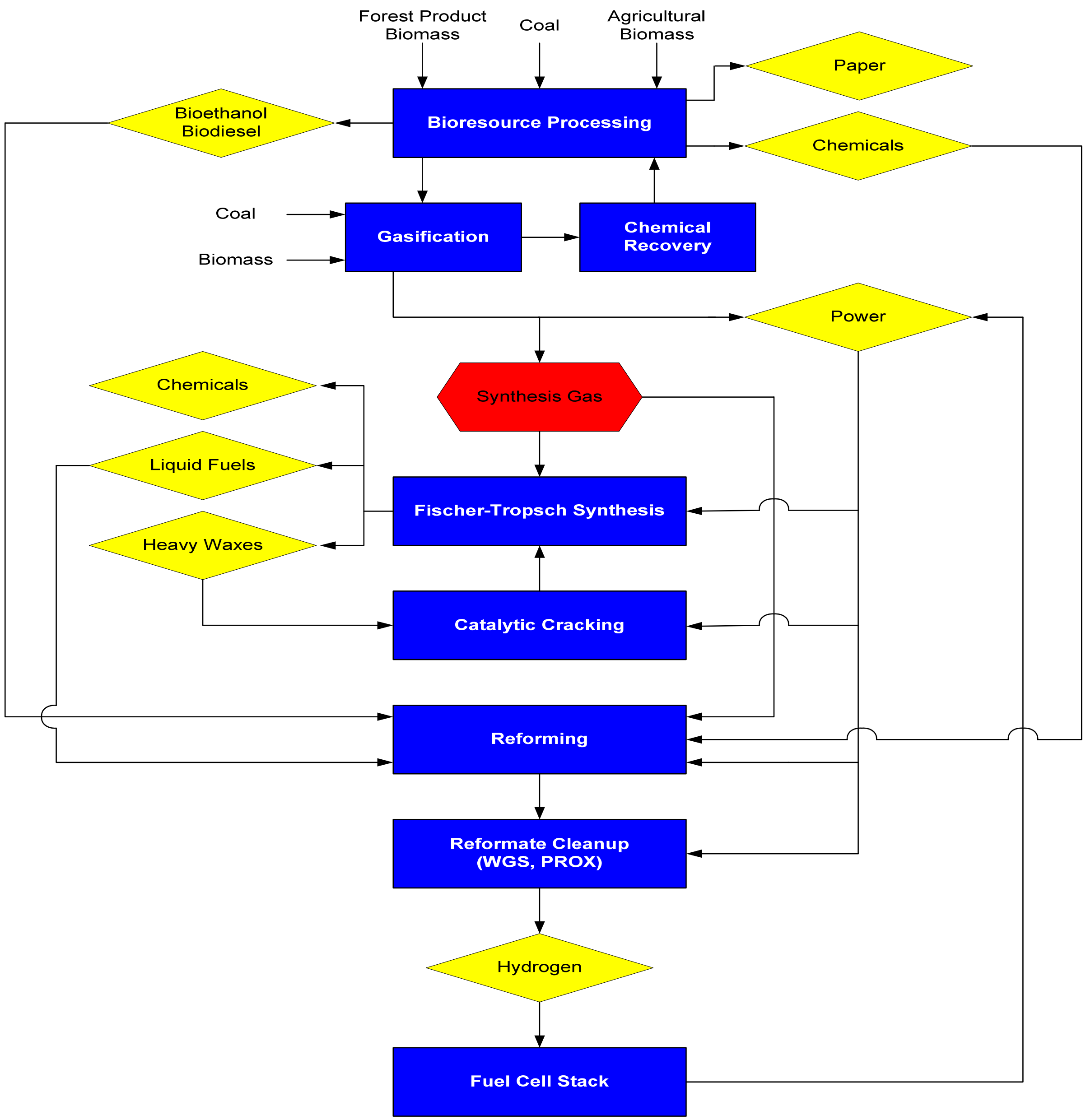
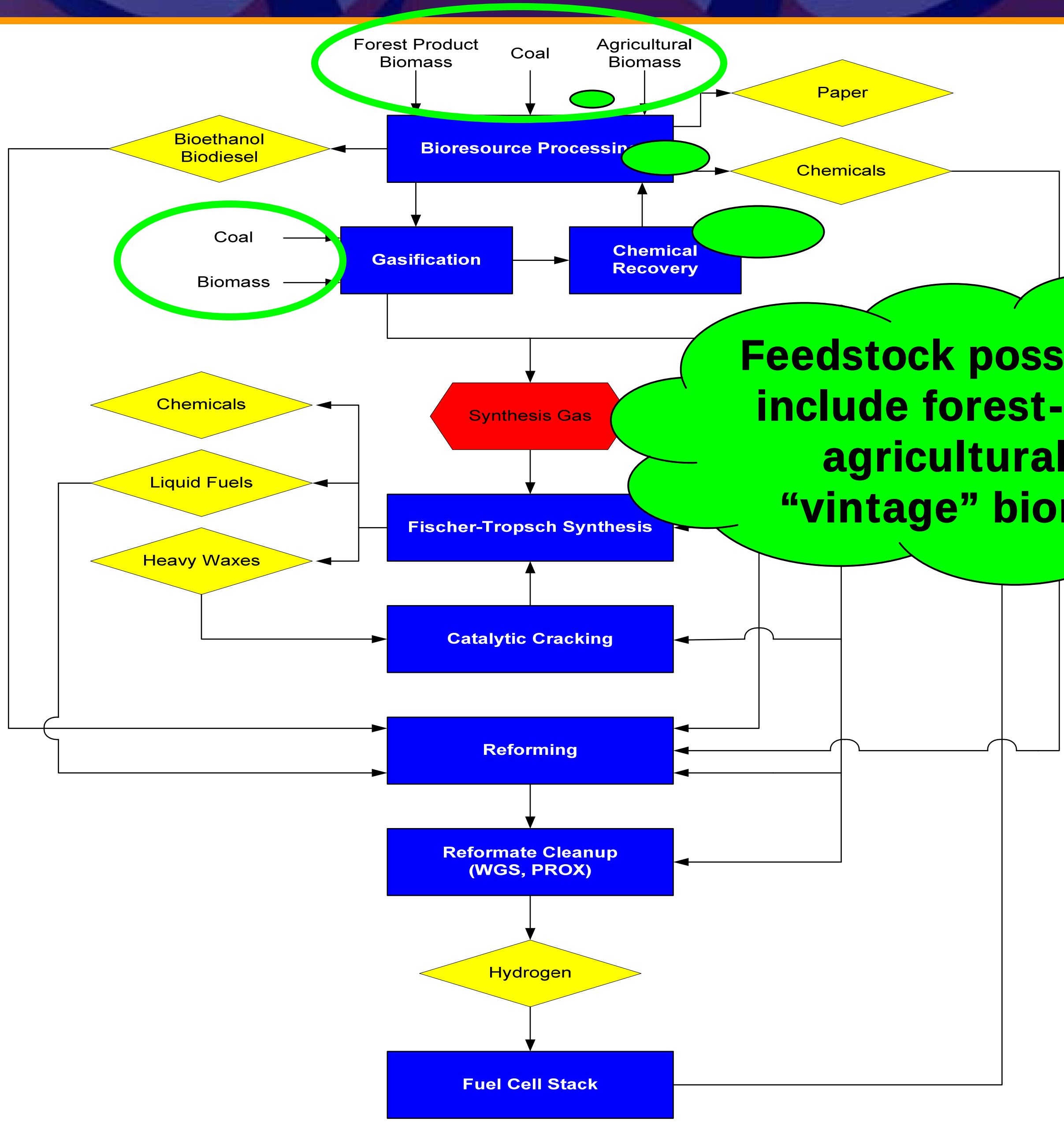


Figure 2: The Forest Biorefinery – Production

Scope of the Problem 1:3

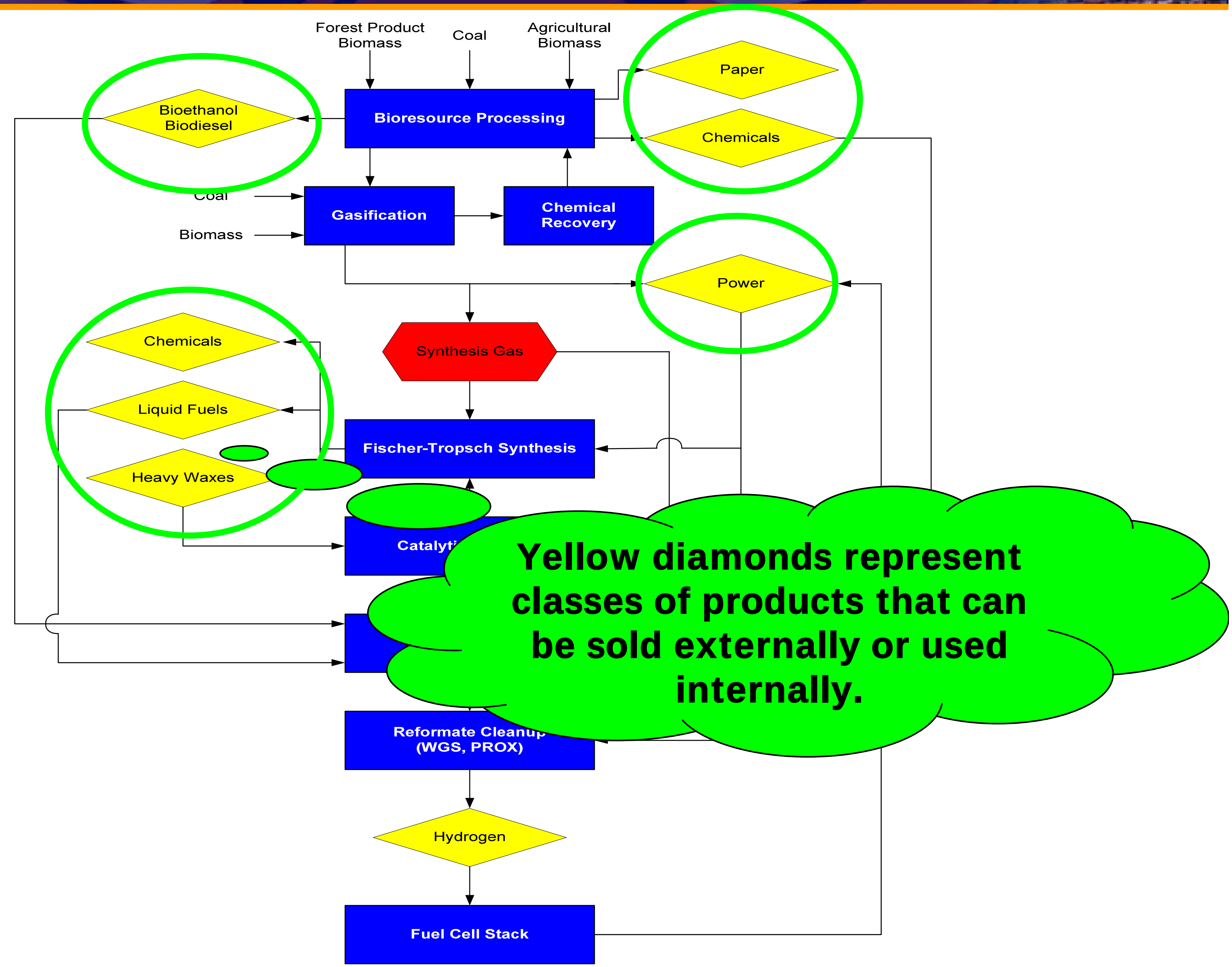


Scope of the Problem 1:3

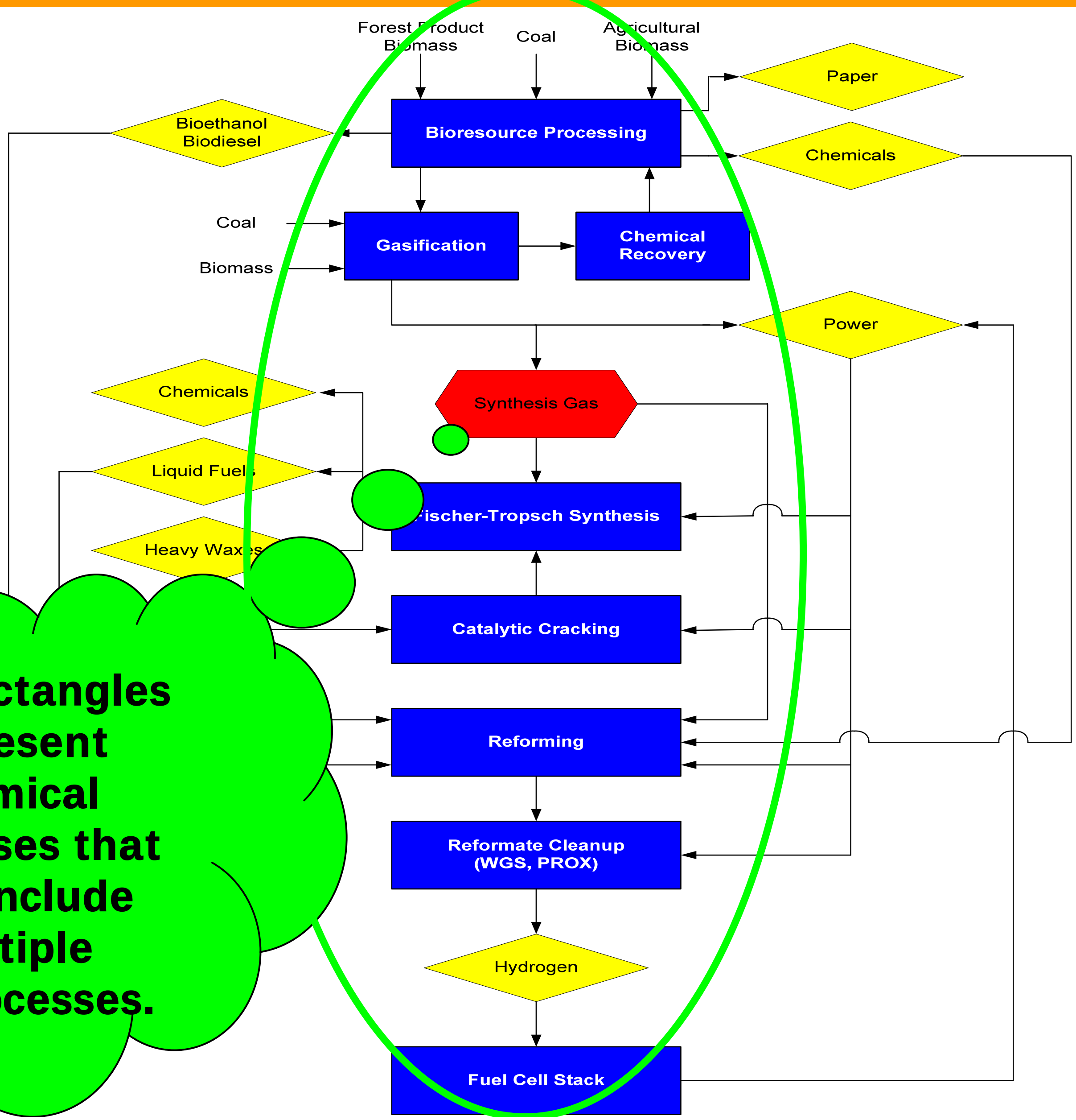


Feedstock possibilities include forest-based, agricultural, or “vintage” biomass.

Scope of the Problem 1:3

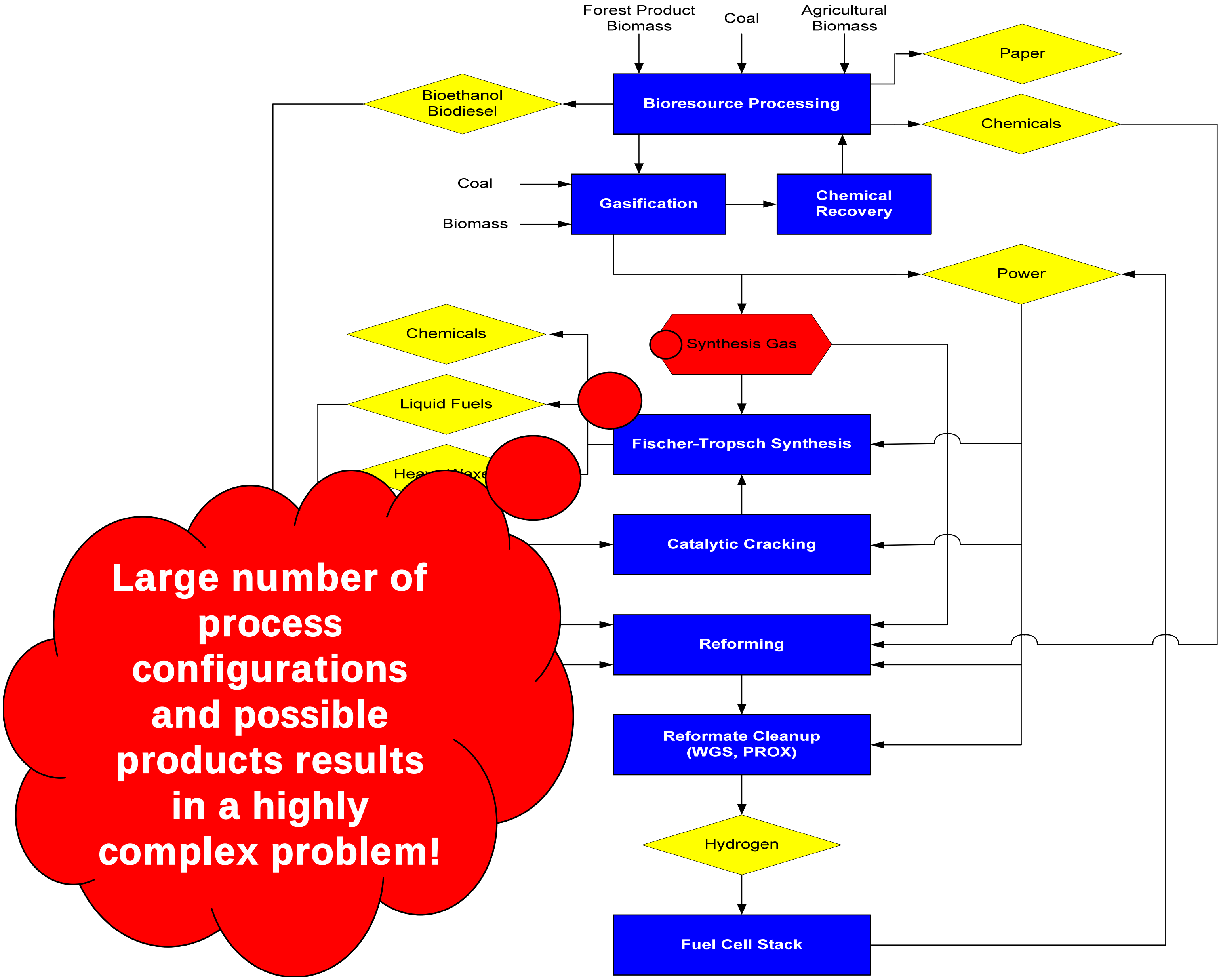


Scope of the Problem 1:3



Blue rectangles represent chemical processes that may include multiple subprocesses.

Scope of the Problem 1:3



Scope of the Problem 2:3

- **Complexity of the Problem**
  - Large number of combinations of process configurations as well as possible products results in a highly complex problem.
  - Decision makers must be able to react to changes in market prices and environmental targets by identifying the optimal product distribution and process configuration.
  - To assist decision makers in this process, it is necessary to develop a framework which includes environmental impact metrics, profitability measures, and other techno-economic metrics.

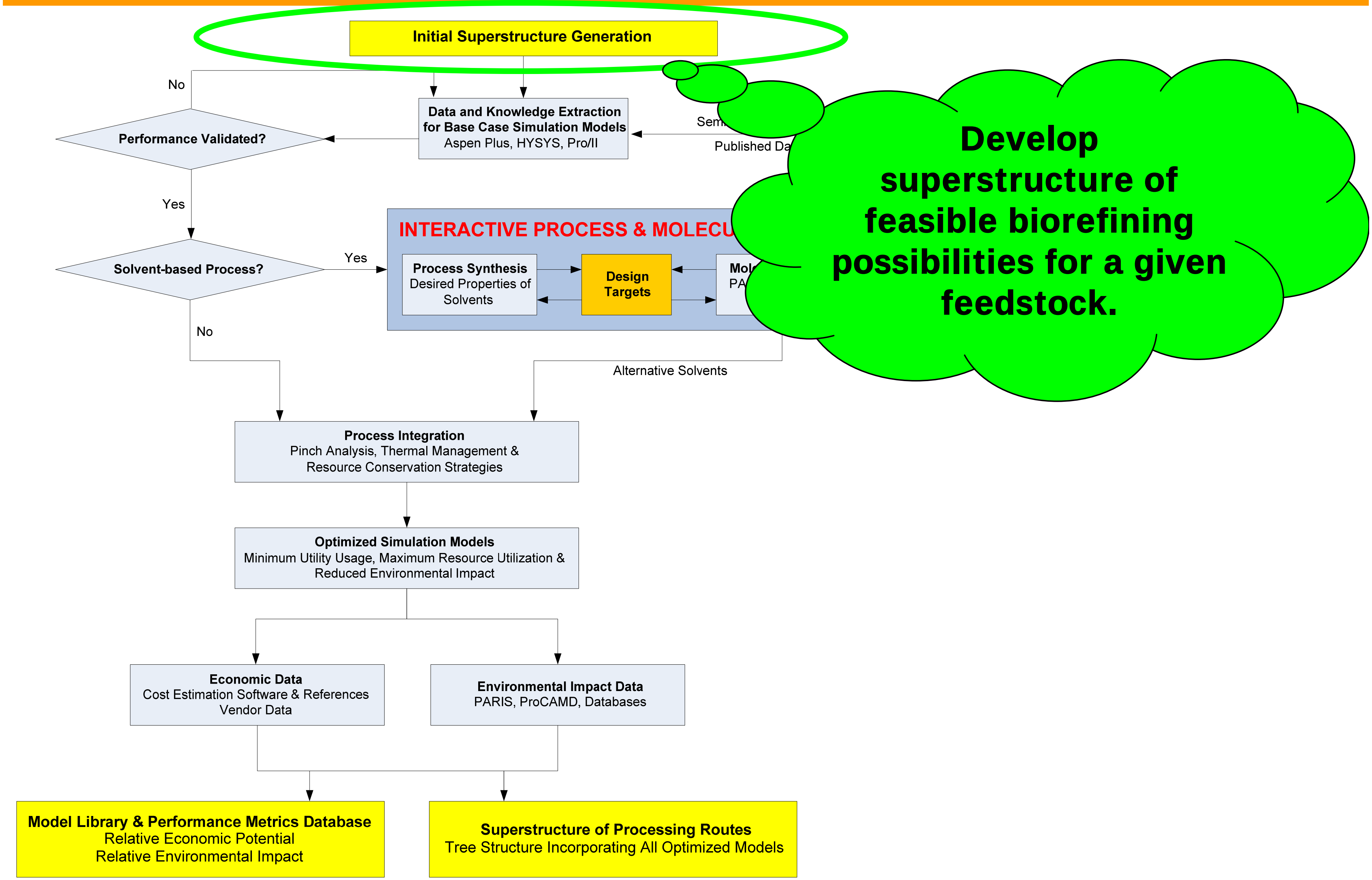
Scope of the Problem 3:3

- **Framework should enable decision makers to answer the following questions:**
  - For a given set of product prices, what should the process configuration be? More specifically, what products should be produced in what amounts?
  - What are the discrete product prices leading to switching between different production schemes?
  - For a given set of desired products, what production route results in the lowest environmental impact?
  - What are the ramifications of changes in supply chain conditions on the optimal process configuration?

Project Objectives 1:1

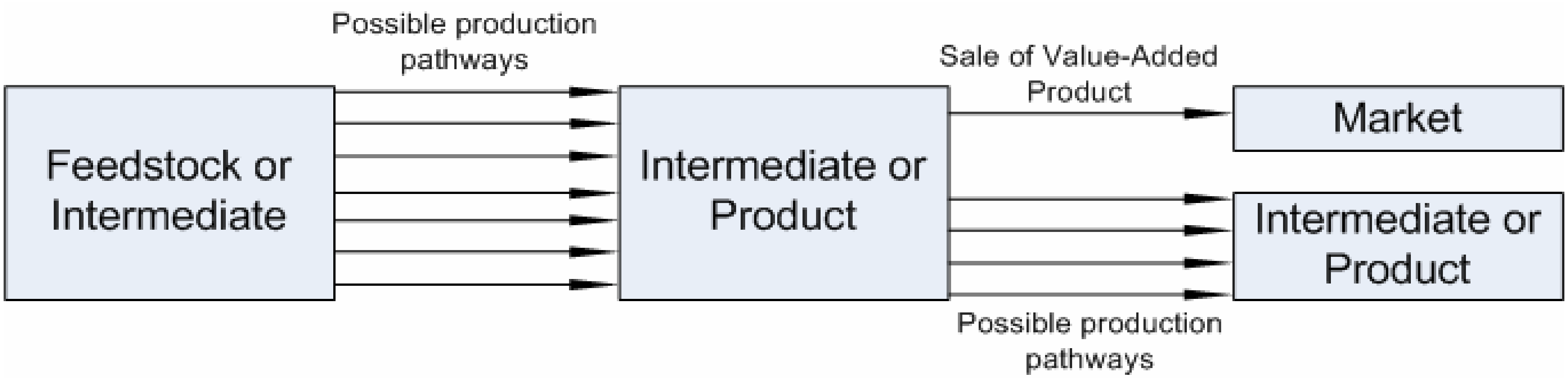
- **Project Objectives**
  - Utilize systematic methods to identify optimal product allocation and processing routes for the emerging field of biorefining
  - Incorporate environmental impact assessment in the design procedure and decision-making process
  - Enhance understanding of the global interactions between the subprocesses and how they impact environmental, technical, and economic performance
  - Incorporate solution into larger problem concerning biorefinery logistics in order to develop a greater understanding concerning the life cycle of biorefining

Problem Approach 1:2



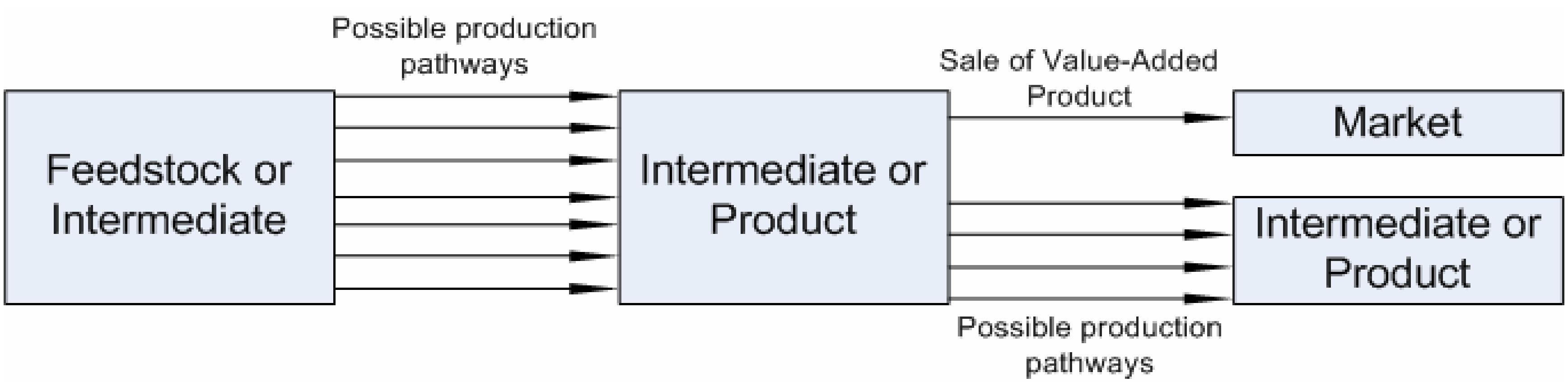
Initial Superstructure Generation 1:3

- **Feedstock to Product Approach**
  - Given a feedstock, determine possible products
    - Existing equipment
    - Available technology
    - Supply chain considerations
  - Determine possible pathways to manufacture products
  - Evaluate salability of products or their possible use as intermediates for value-added products



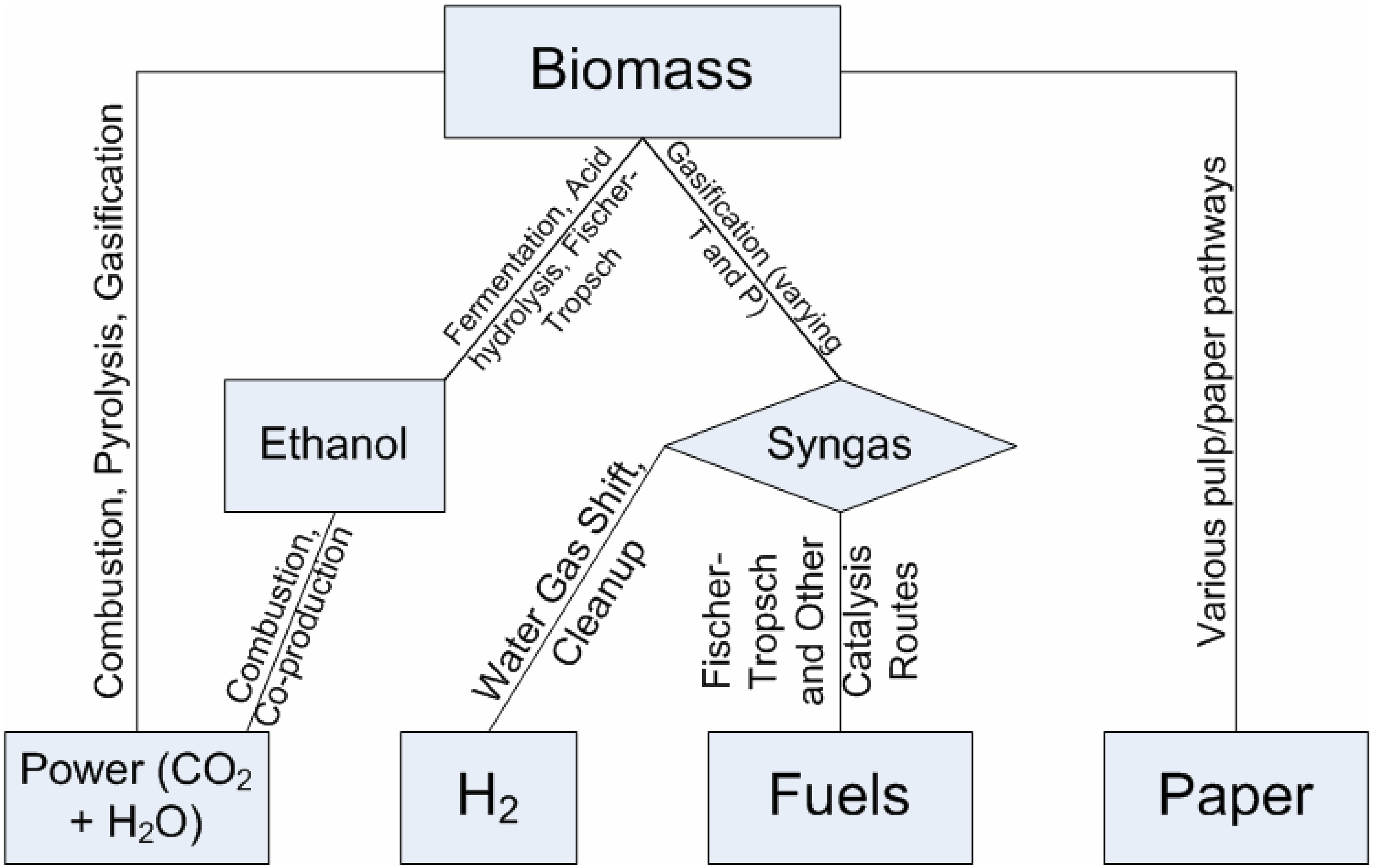
Initial Superstructure Generation 2:3

- **Product from Feedstock Approach**
  - Given a product, determine possible feedstocks
    - Existing equipment
    - Available technology
    - Supply chain considerations
  - Determine possible pathways to manufacture products
  - Evaluate whether the feed for targeted process is an intermediate from bio-based process or a raw material

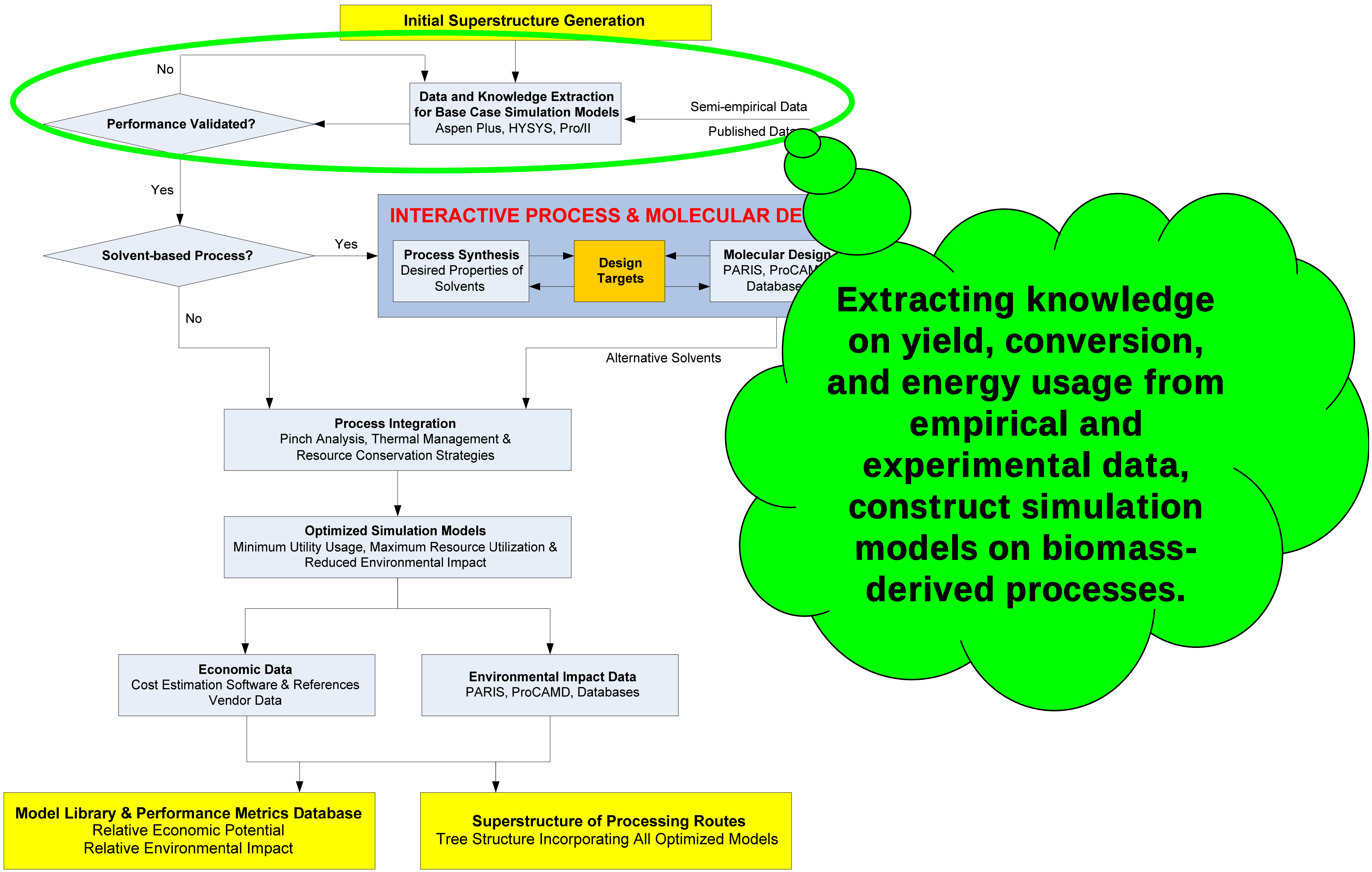


Initial Superstructure Generation 3:3

- **Example**



Problem Approach 1:2



Basic Simulation Models 1:3

- **For basic simulation models**
  - Develop all models on a consistent basis
    - Terms of feedstock flow or desired product flow
    - Run at consistent percentage of capacity (e.g. 80%)
  - Note main equipment needed
    - Preparation, main process, separation
    - Use black box models if details are unavailable
  - Limit number of process combinations
    - Use "high" or "low" temperature/pressure instead of a range of different operating temperature/pressures
    - Look at using different classes of catalysts instead of numerous individual ones

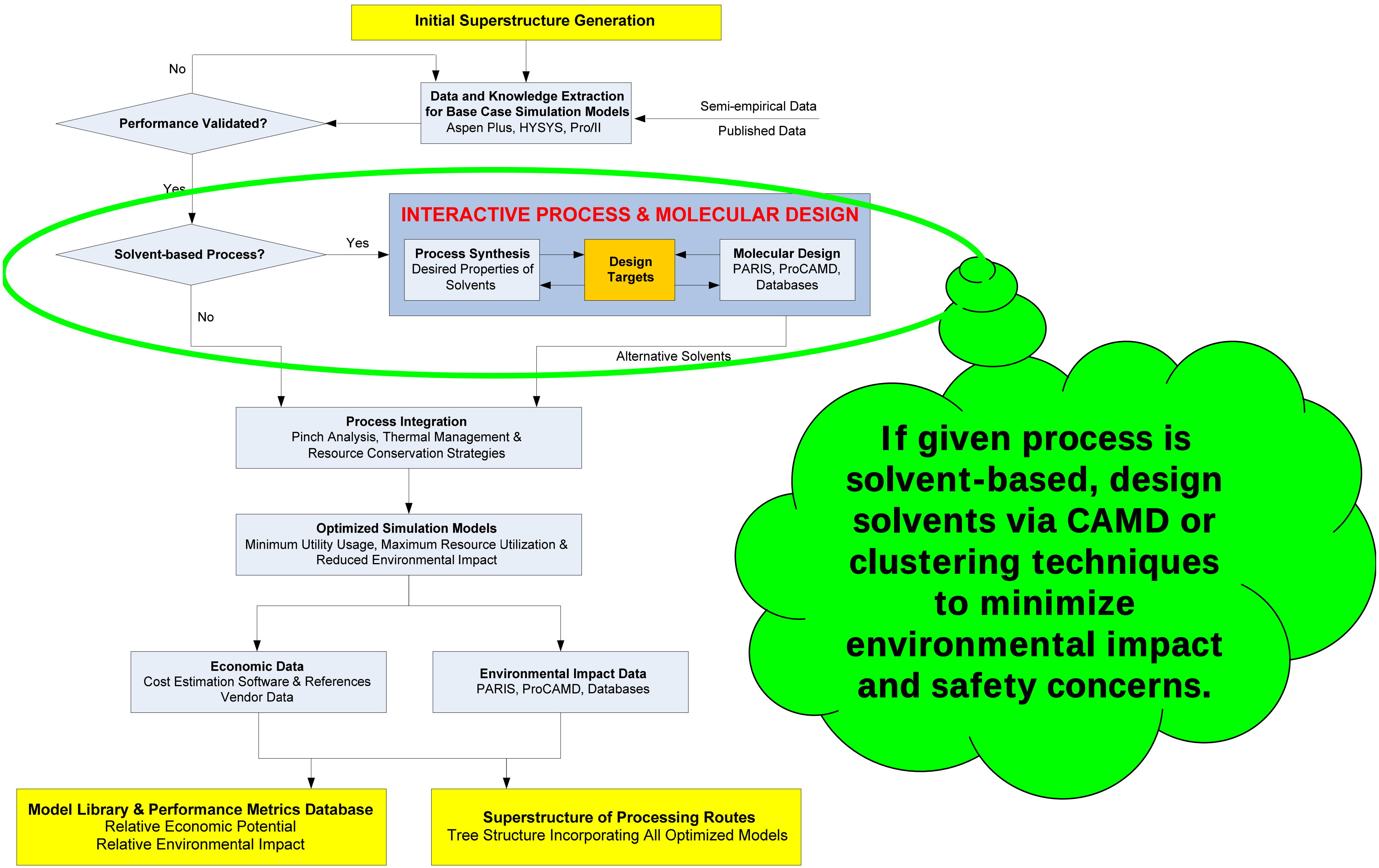
Basic Simulation Models 2:3

- **Information needed from models**
  - Total fixed cost
    - Use established methodology such as Peters and Timmerhaus to determine total equipment cost
  - Conversion rate (output per input)
    - Implement unit conversions (e.g. X gallons of ethanol per Y bone dry tons biomass)
  - Heating and cooling utility usage (pre-integration)
  - Variable cost per unit output
    - Include separation cost (heating, cooling, power, regeneration)
  - Outlet composition after separation
    - Product streams and effluent streams

Basic Simulation Models 3:3

- **Black box advantages**
  - Speed and simplicity
  - Ability to tackle more process configurations at once
  - May evaluate newer technologies in which details are not yet available
- **Detailed model advantages**
  - More robust solutions
  - Potential to uncover hidden inefficiencies in details
  - Ability to utilize process integration in order to decrease variable and fixed costs

Problem Approach 1:2



CAMD 1:3

Property prediction:

Given:
Information on compound structure.

→

Obtained:
Properties of the compound.

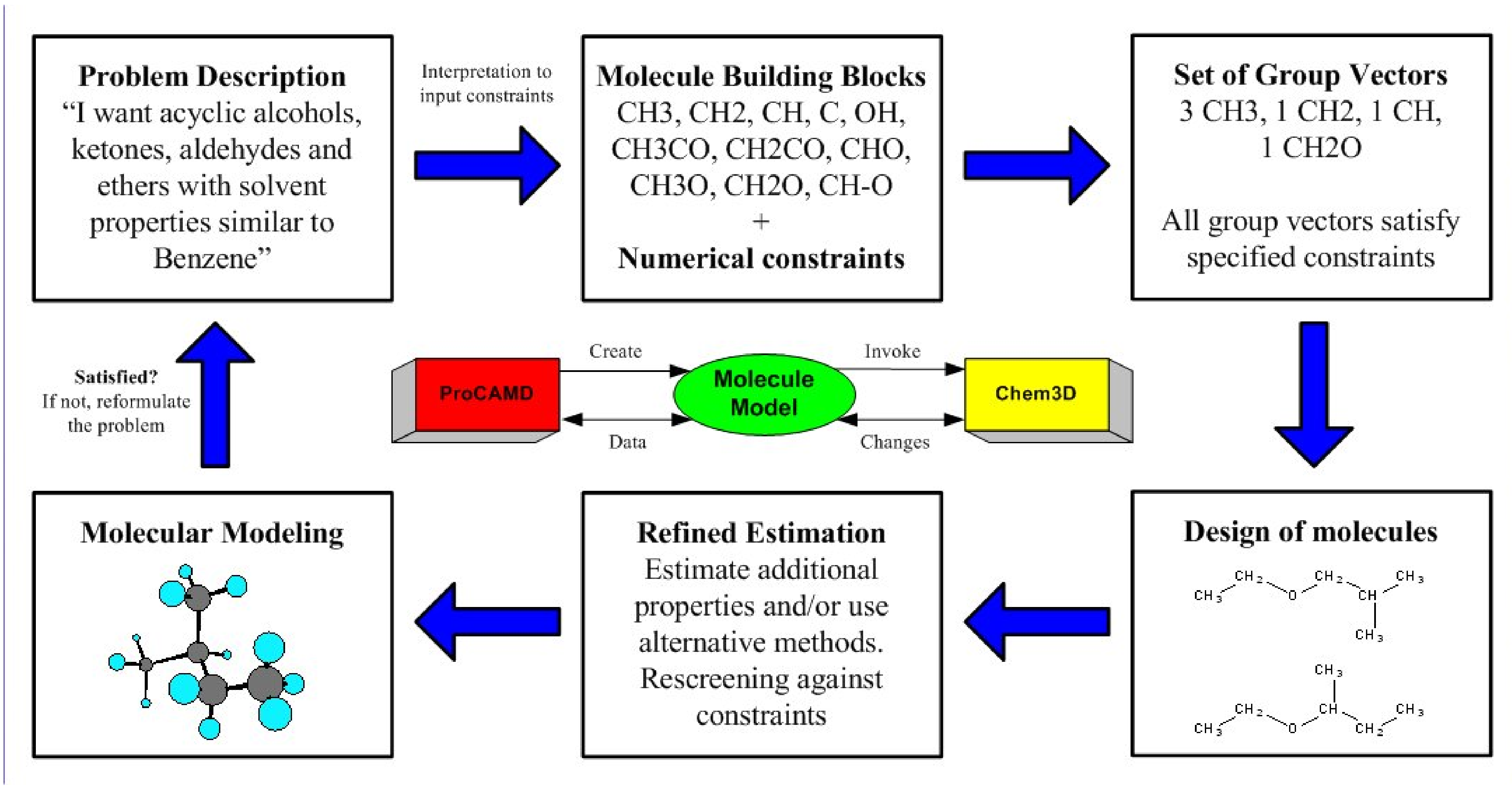
Computer Aided Molecular Design:

Given:
Information on desired properties & type of compound.

→

Obtained:
Compound structures having the desired properties.

CAMD 2:3


Problem Description
"I want acyclic alcohols, ketones, aldehydes and ethers with solvent properties similar to Benzene"
Interpretation to input constraints
Molecule Building Blocks
CH3, CH2, CH, C, OH, CH3CO, CH2CO, CHO, CH3O, CH2O, CH-O
+
Numerical constraints
Set of Group Vectors
3 CH3, 1 CH2, 1 CH, 1 CH2O
All group vectors satisfy specified constraints
Satisfied?
If not, reformulate the problem
ProCAMD
Create
Data
Molecule Model
Invoke
Changes
Chem3D
Molecular Modeling
Refined Estimation
Estimate additional properties and/or use alternative methods. Rescreening against constraints
Design of molecules

CAMD 3:3

- **Application Examples**
  - Water/phenol system: Toluene replacement
  - Separation of Cyclohexane and Benzene
  - Separation of Acetone and Chloroform
  - Refrigerants for heat pump systems
  - Heat transfer fluids for heat recovery and storage
  - and many others

Aniline Case Study 1:7

- **Problem Description**
  - During the production of a pharmaceutical, aniline is formed as a byproduct. Due to strict product specifications the aniline content of an aqueous solution has to be reduced from 28000 ppm to 2 ppm.

- **Conventional Approach**
  - Single stage distillation.
  - Reduces aniline content to 500 ppm.
  - Energy usage: 4248.7 MJ
  - No data is available for the subsequent downstream processing steps.

Aniline Case Study 2:7

- **Objective**
  - Investigate the possibility of using liquid-liquid extraction as an alternative unit operation by identification of a feasible solvent

- **Reported Aniline Solvents**
  - Water, Methanol, Ethanol, Ethyl Acetate, Acetone

Property	Aniline	Water
CAS No.	62–53–3	7732–18–5
Boiling Point (K)	457.15	373.15
Solubility Parameter ($MPa^{1/2}$)	24.12	47.81

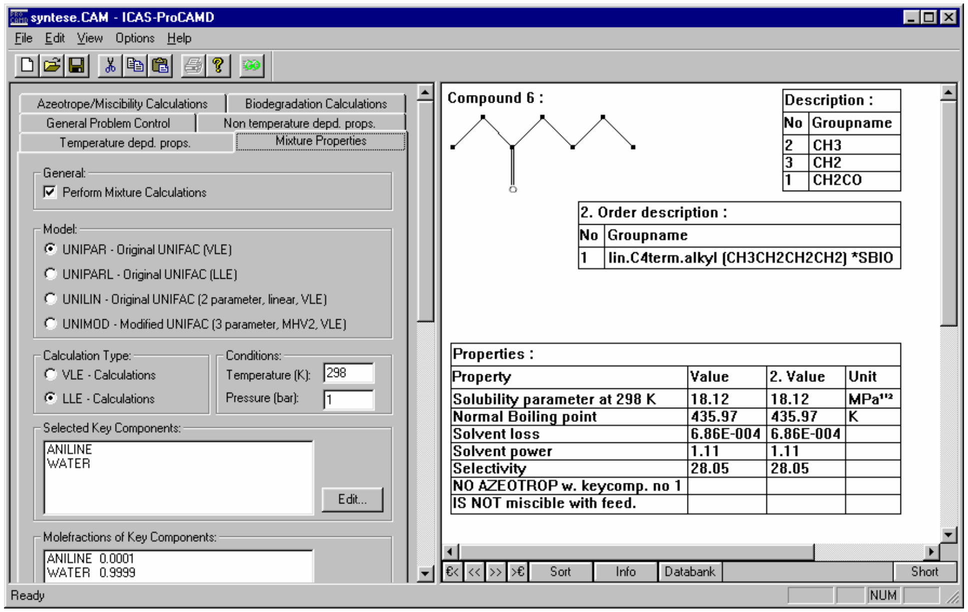
Aniline Case Study 3:7

- **Performance of Solvent**
  - Liquid at ambient temperature
  - Immiscible with water
  - No azeotropes between solvent & aniline and/or water
  - High selectivity with respect to aniline
  - Minimal solvent loss to water phase
  - Sufficient difference in boiling points for recovery
- **Structural and EH&S Aspects**
  - No phenols, amines, amides or polyfunctional compounds.
  - No compounds containing double/triple bonds.
  - No compounds containing Si, F, Cl, Br, I or S

Aniline Case Study 4:7

- **Results of Solvent Search**
  - No high boiling solvents found

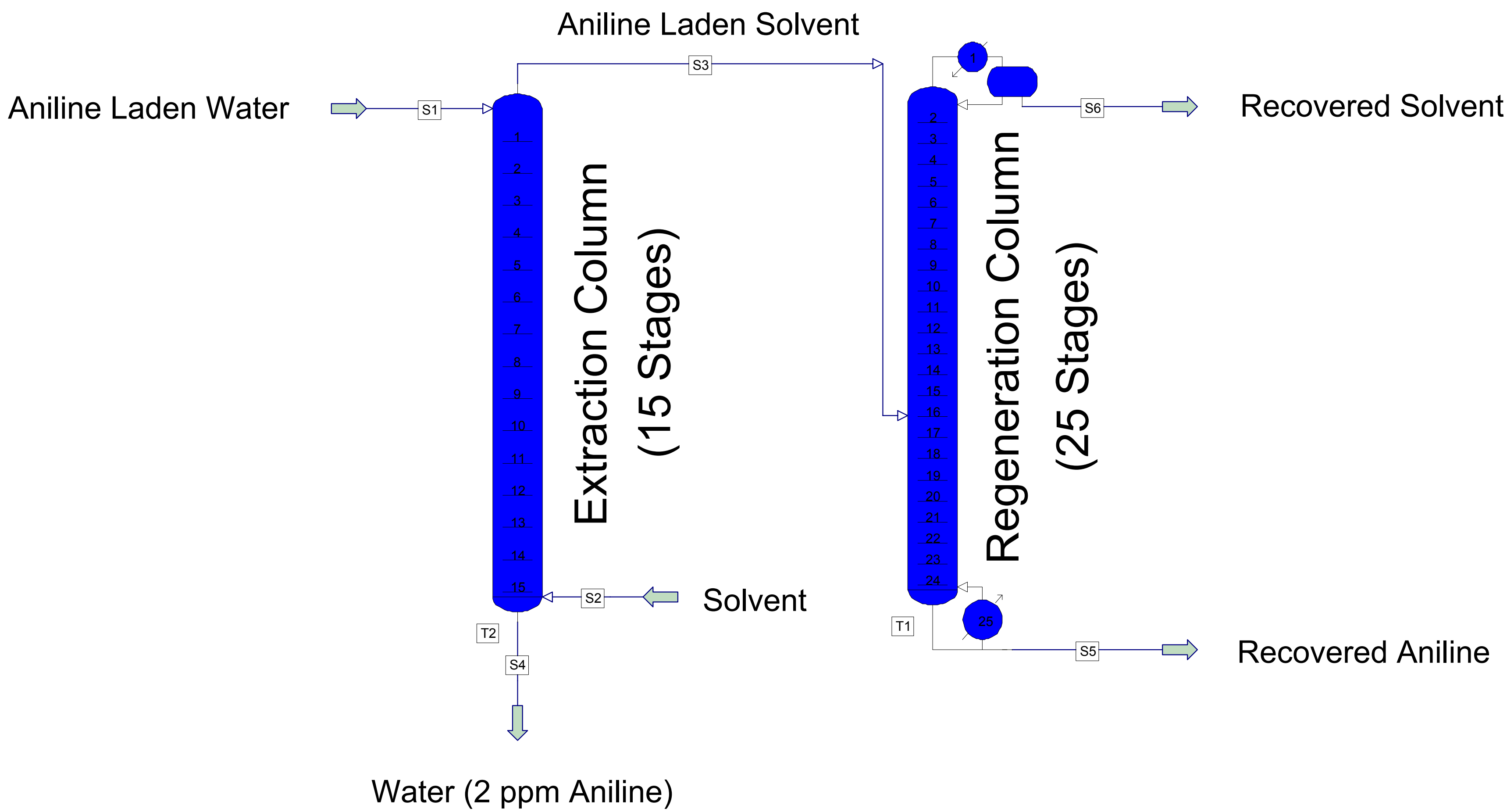
Also, higher and branched alkanes were identified as candidates



Solvent	CAS No.
n-Octane	111–65–9
2-Heptanone	110–43–0
3-Heptanone	106–35–4

Aniline Case Study 5:7

- **Process Simulation**



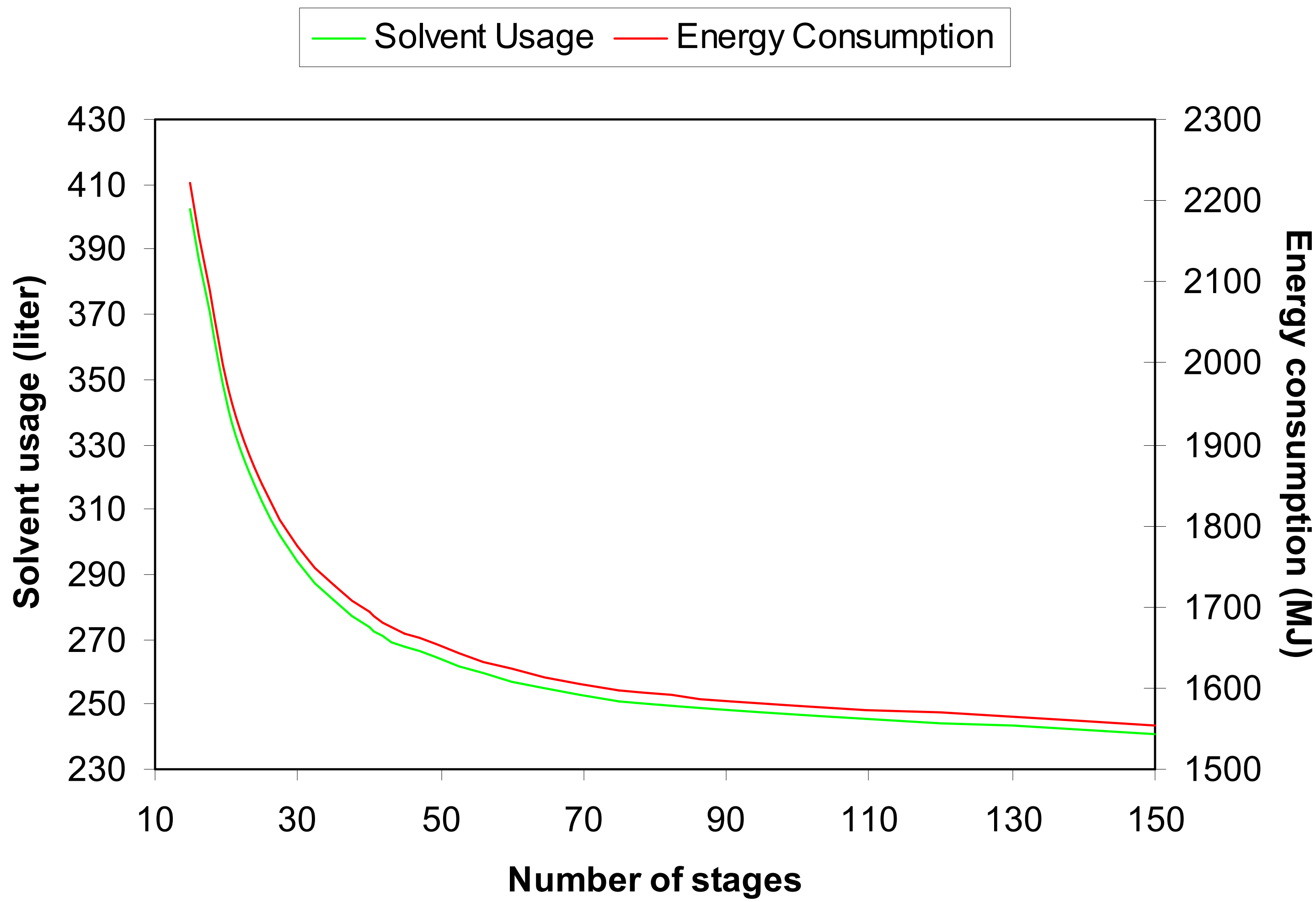
Aniline Case Study 6:7

- **Performance Targets and Results**
  - Countercurrent extraction and simple distillation.
  - Terminal concentration of 2 ppm aniline in water phase.
  - Highest possible purity during solvent regeneration

Design Parameter	n-Octane	2-Heptanone	3-Heptanone
Solvent amount (mole)	2488.8	1874.0	1873.5
Solvent amount (kg)	284.3	214.0	213.9
Solvent amount (liter)	402.6	261.2	260.9
Solvent amount in water phase (mol)	0.0341	161.2	161.2
Solvent amount in water phase (ppm)	1	429	429
Aniline product purity (weight%)	100.00	100.00	100.00
Recovery of aniline from solvent (%)	100.00	99.95	99.99
Solvent loss (% on a mole basis)	0.00098	8.60	8.60
Energy consumption for solvent recovery	2.223	2.245	2.009

Aniline Case Study 7:7

- **Validation of Minimum Cost Solution**



Oleic Acid Methyl Ester 1:3

- **Problem Description**
  - Fatty acid used in a variety of applications, e.g. textile treatment, rubbers, waxes, and biochemical research
  - Reported solvents: Diethyl Ether, Chloroform

Volatile
Flammable

Carcinogen

- **Goal**
  - Identify alternative solvents with better safety and environmental properties.

Oleic Acid Methyl Ester 2:3

- **Solvent Specification**
  - Liquid at normal (ambient) operating conditions.
  - Non-aromatic and non-acidic (stability of ester).
  - Good solvent for Oleic acid methyl ester.

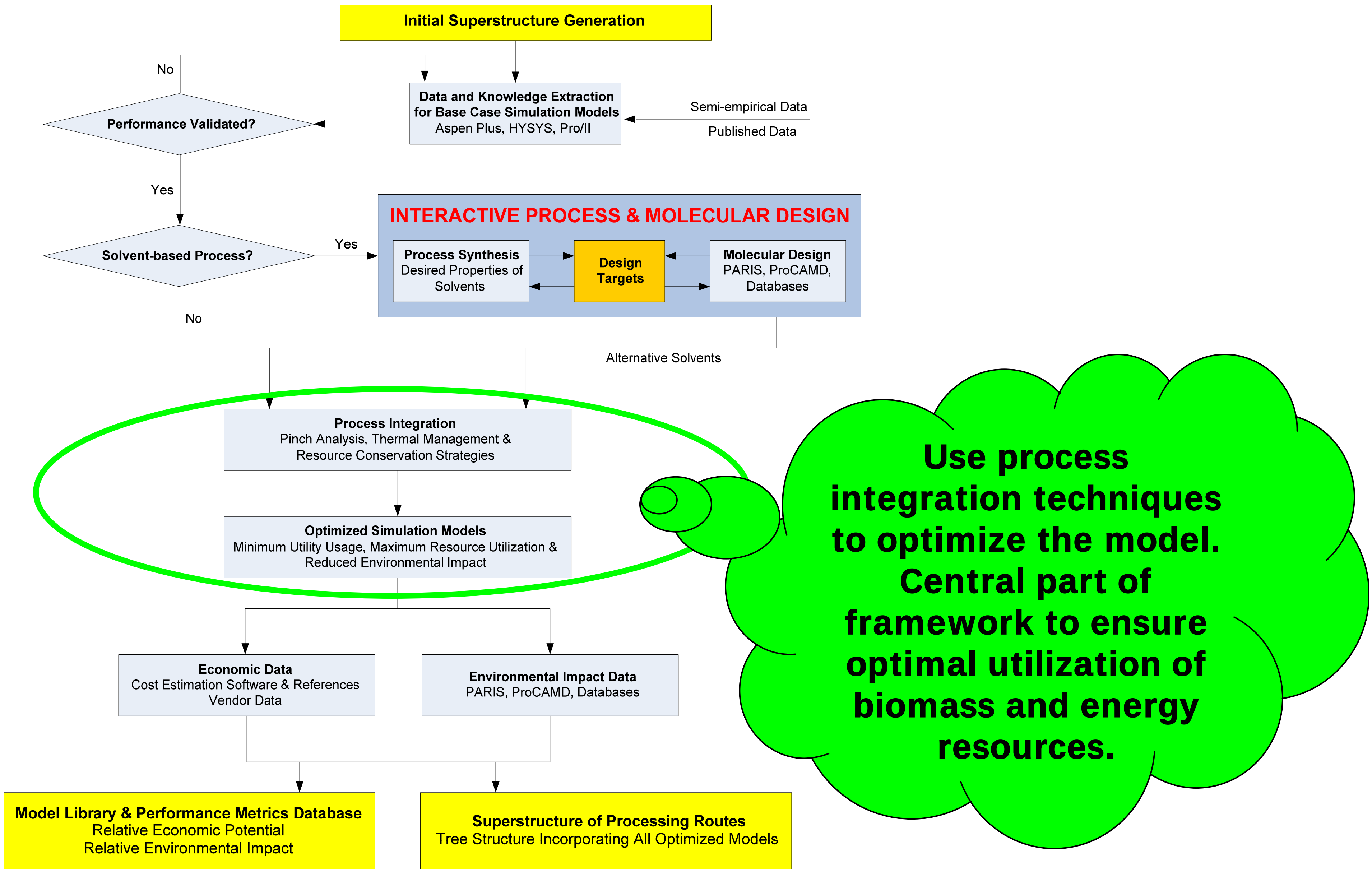
- **Constraints**
  - Melting Point (T_m) < 280K
  - Boiling Point (T_b) > 340K
  - Acyclic compounds containing no Cl, Br, F, N or S
  - Octanol/Water Partition coefficient (logP) < 2
  - $15.95\ (MPa)^{1/2} < \delta < 17.95\ (MPa)^{1/2}$

Oleic Acid Methyl Ester 3:3

- **Database Approach (2 Candidates)**
  - 2-Heptanone
  - Diethyl Carbitol

- **CAMD Approach (1351 Compounds Found)**
  - Maximum of two functional groups allowed, thus avoiding complex (and expensive) compounds.
  - Formic acid 2,3-dimethyl-butyl ester
  - 3-Ethoxy-2-methyl-butyraldehyde
  - 2-Ethoxy-3-methyl-butyraldehyde
  - Calculation time approximately 45 sec on standard PC.

Problem Approach 1:2



Heat Integration Overview

- Early pioneers
  - Rudd @ Wisconsin (1968)
  - Hohmann @ USC (1971)
- Central figure
  - Linnhoff @ ICI/UMIST (1978)
  - Currently: President, Linnhoff-March
- Recommended text
  - Seider, Seader and Lewin (2004): Product and Process Design Principles, 2 ed. Wiley and Sons, NY
  - Linnhoff et al. (1982): A User Guide on Process Integration for the Efficient Use of Energy, I. Chem. E., London
- Most comprehensive review:
  - Gundersen, T. and Naess, L. (1988): The Synthesis of Cost Optimal Heat Exchanger Networks: An Industrial Review of the State of the Art, Comp. Chem. Eng., 12(6), 503-530

Heat Integration Basics

- The design of Heat Exchanger Networks (**HENs**) deals with the following problem:

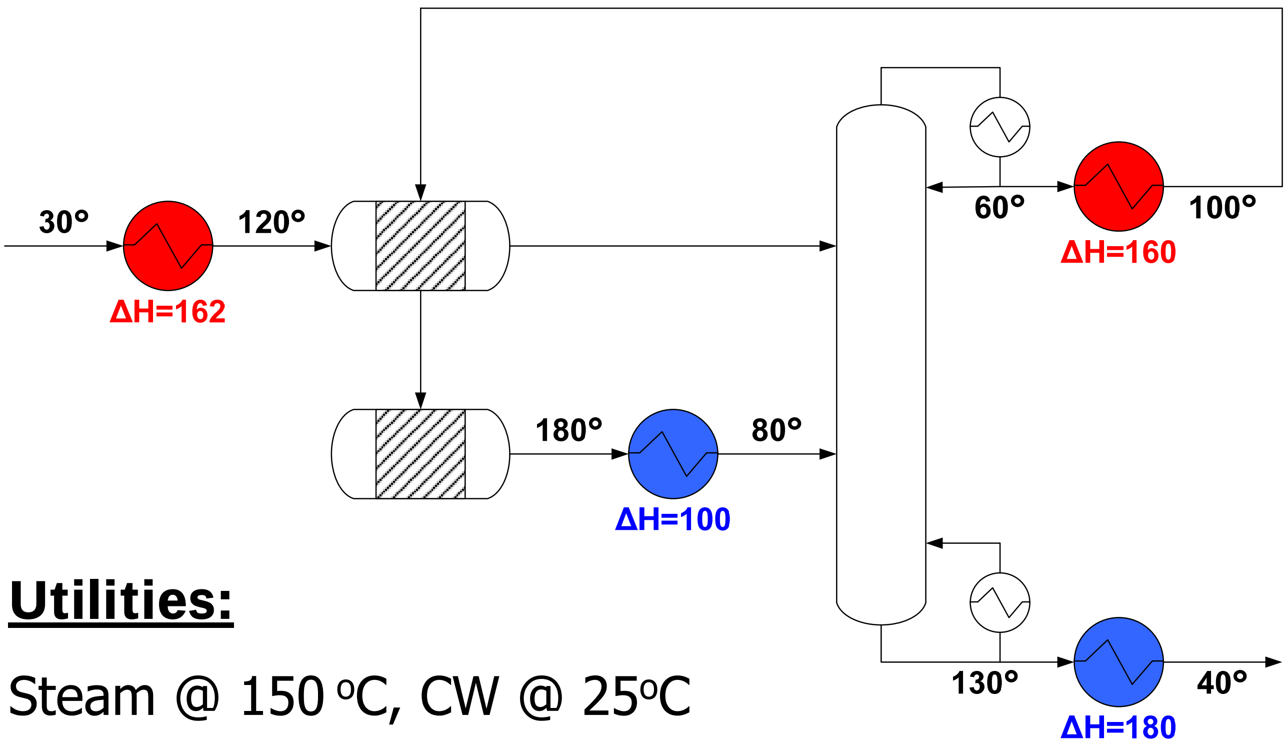
Given:

- N_H hot streams, with given heat capacity flowrate, each having to **be cooled** from supply temperature T_H^S to targets T_H^T
- N_C cold streams, with given heat capacity flowrate, each having to **be heated** from supply temperature T_C^S to targets T_C^T

Design:

An optimum network of heat exchangers, connecting between the hot and cold streams and between the streams and cold/hot utilities (furnace, hot-oil, steam, cooling water or refrigerant, depending on the required duty temperature)

Simple Example



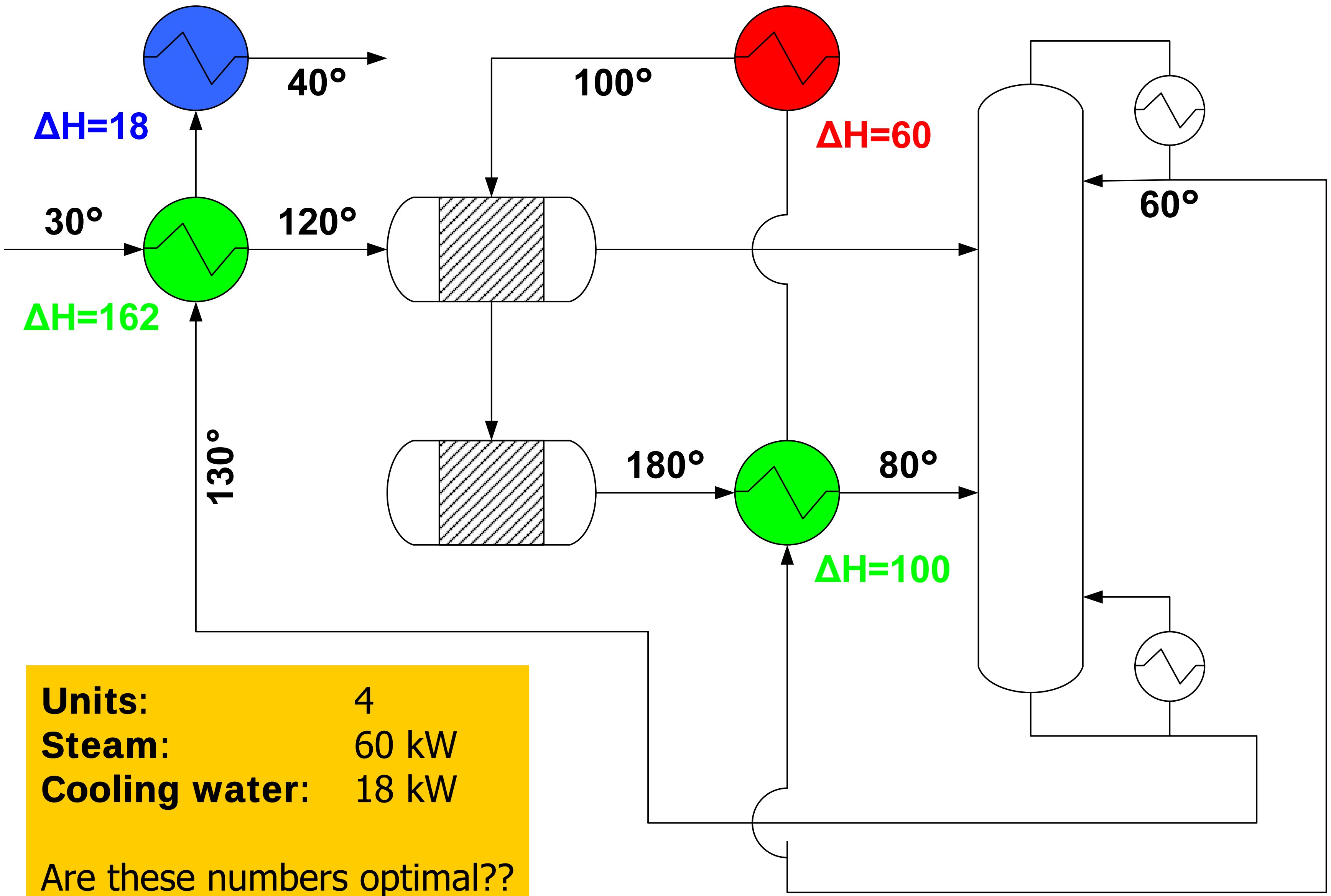
Utilities:

Steam @ 150 °C, CW @ 25°C

Stream	T^S (°C)	T^T (°C)	ΔH (kW)	CP (kW/°C)
H1	180	80	100	1.0
H2	130	40	180	2.0
C1	60	100	160	4.0
C2	30	120	162	1.8

Design a network of steam heaters, water coolers and exchangers for the process streams. Where possible, use exchangers in preference to utilities.

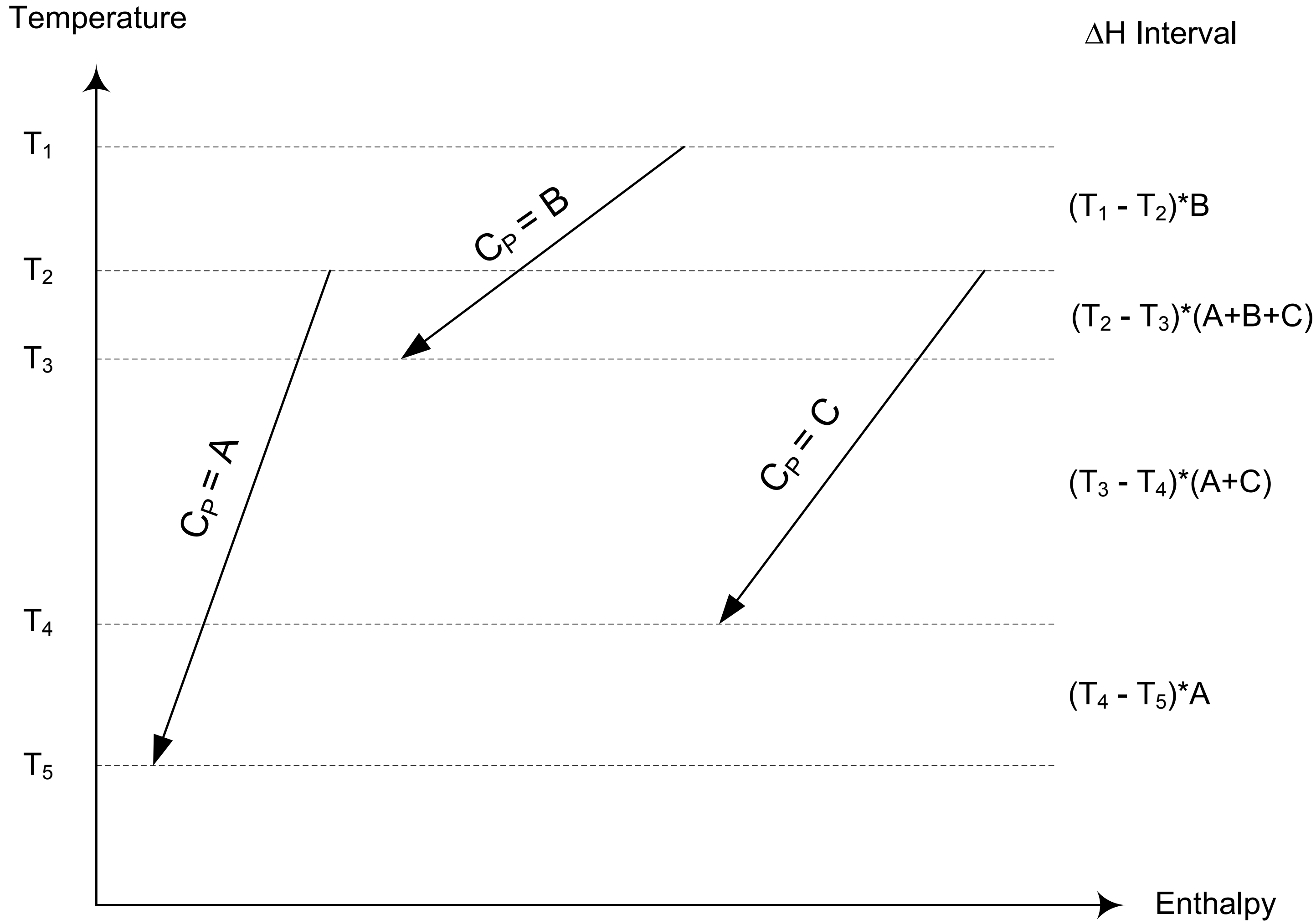
Simple Example - Targets



Units: 4
Steam: 60 kW
Cooling water: 18 kW

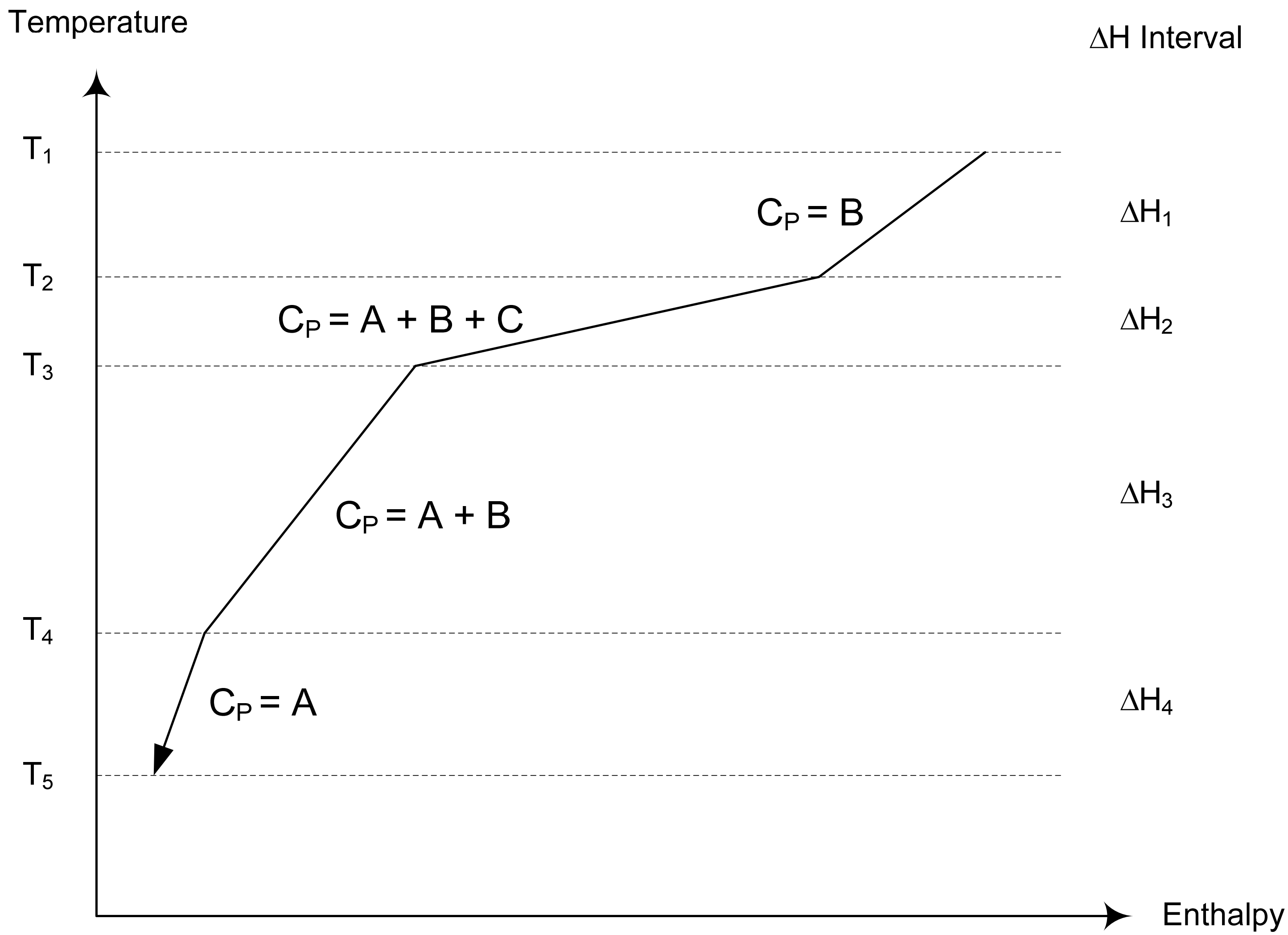
Are these numbers optimal??

The Composite Curve 1:2



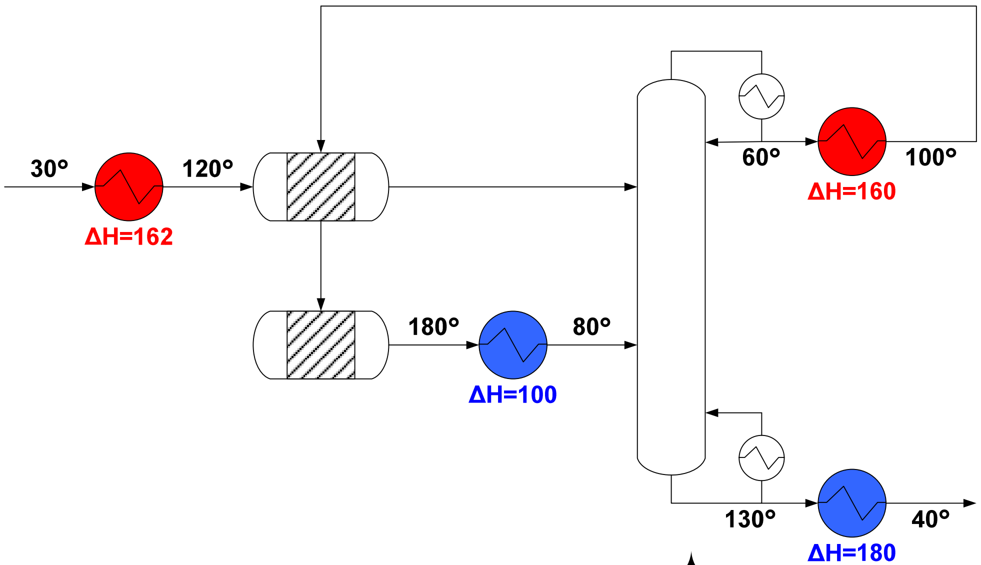
Three (3) hot streams

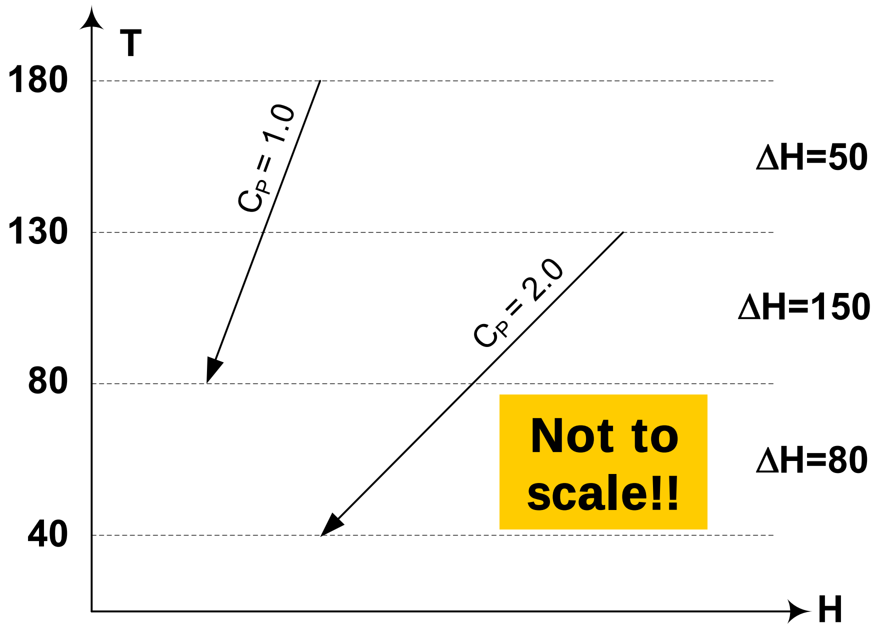
The Composite Curve 2:2

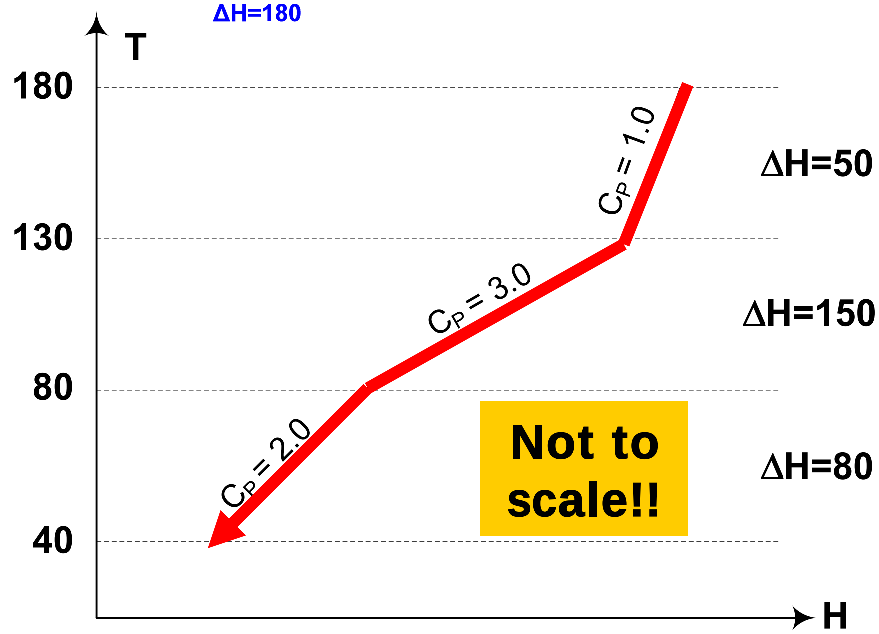


Three (3) hot streams

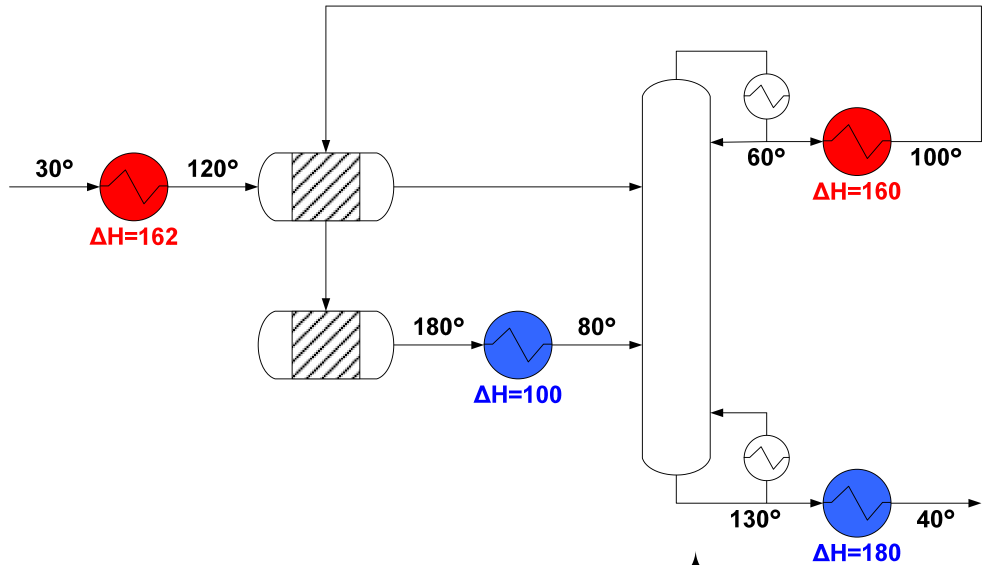
Simple Ex. – Hot Composite

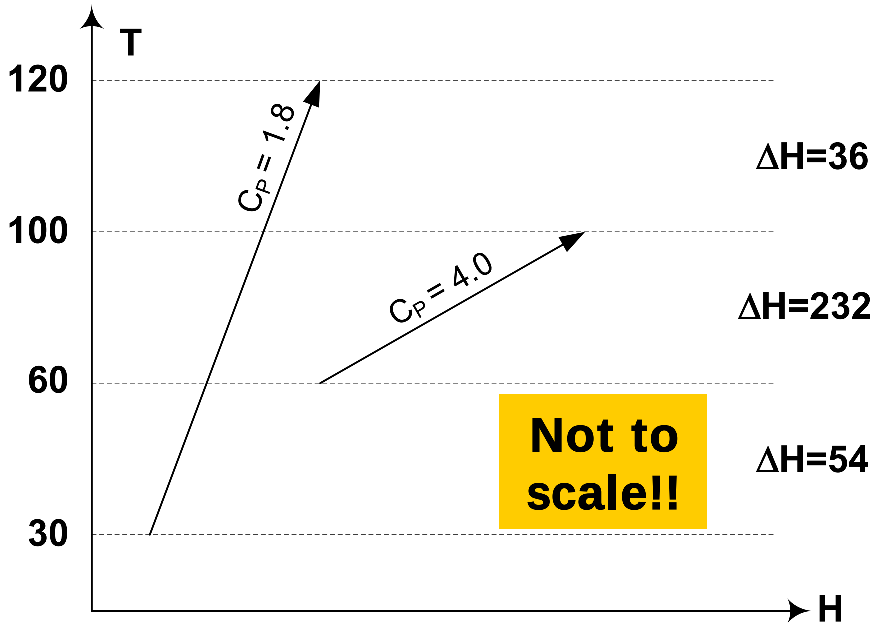


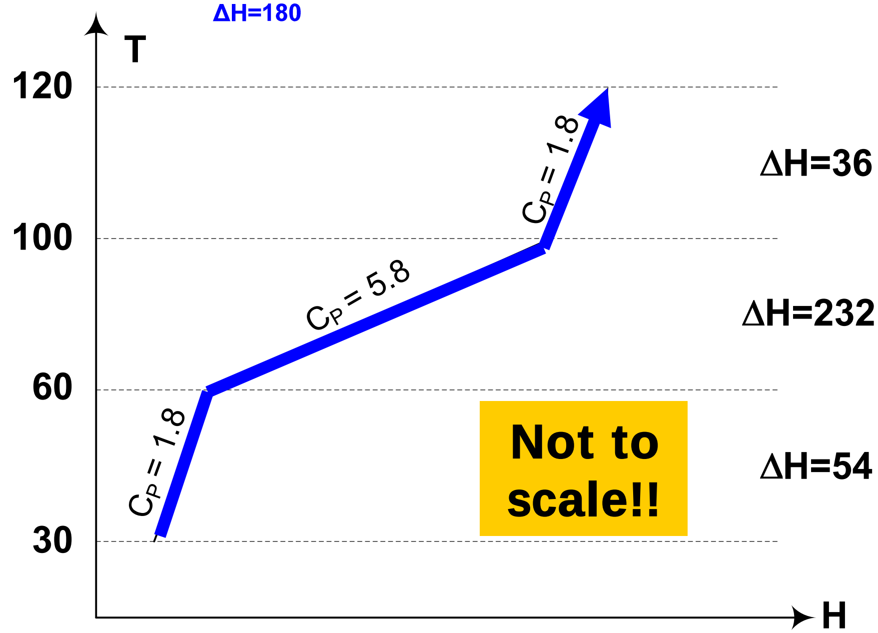




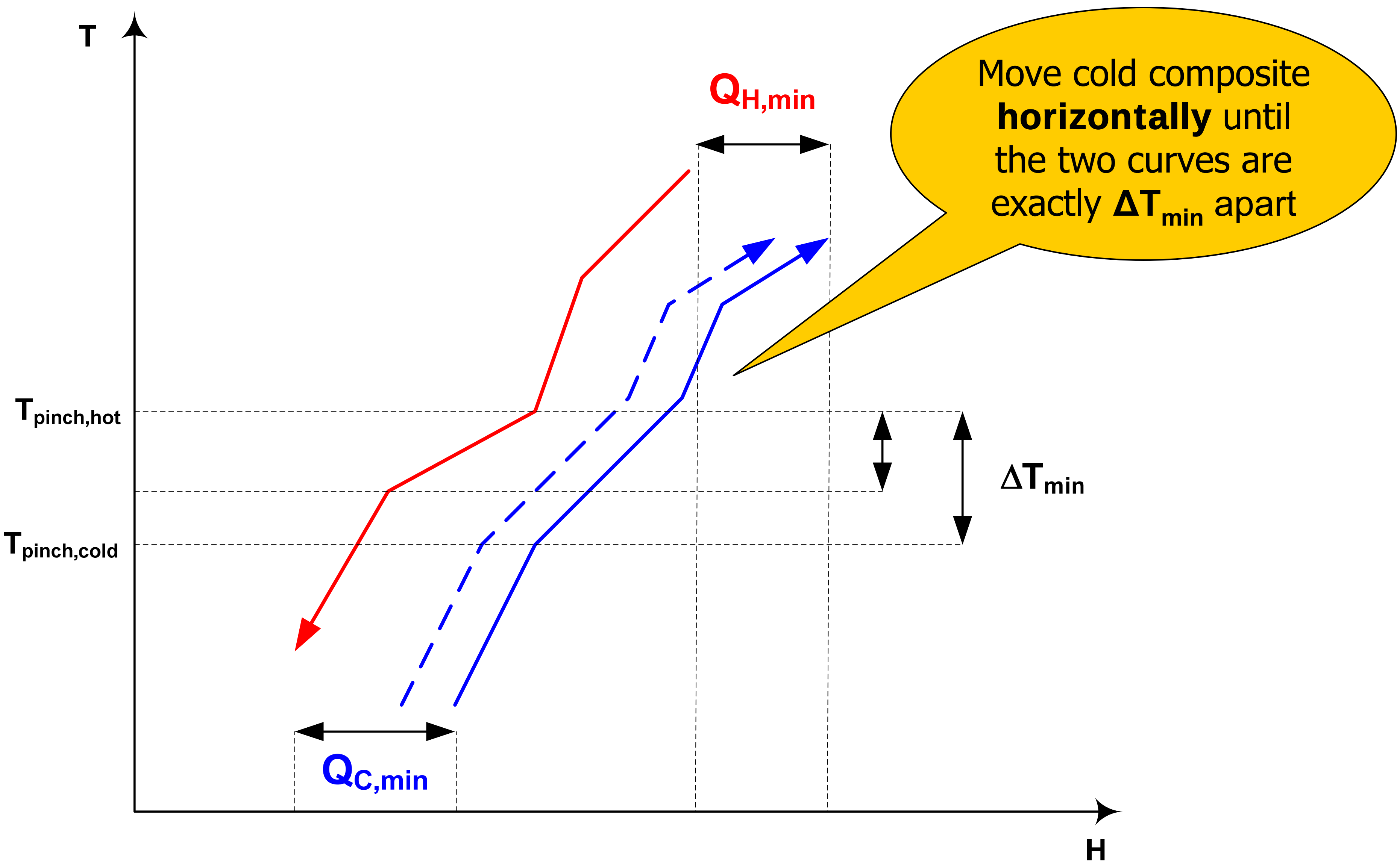
Simple Ex. – Cold Composite



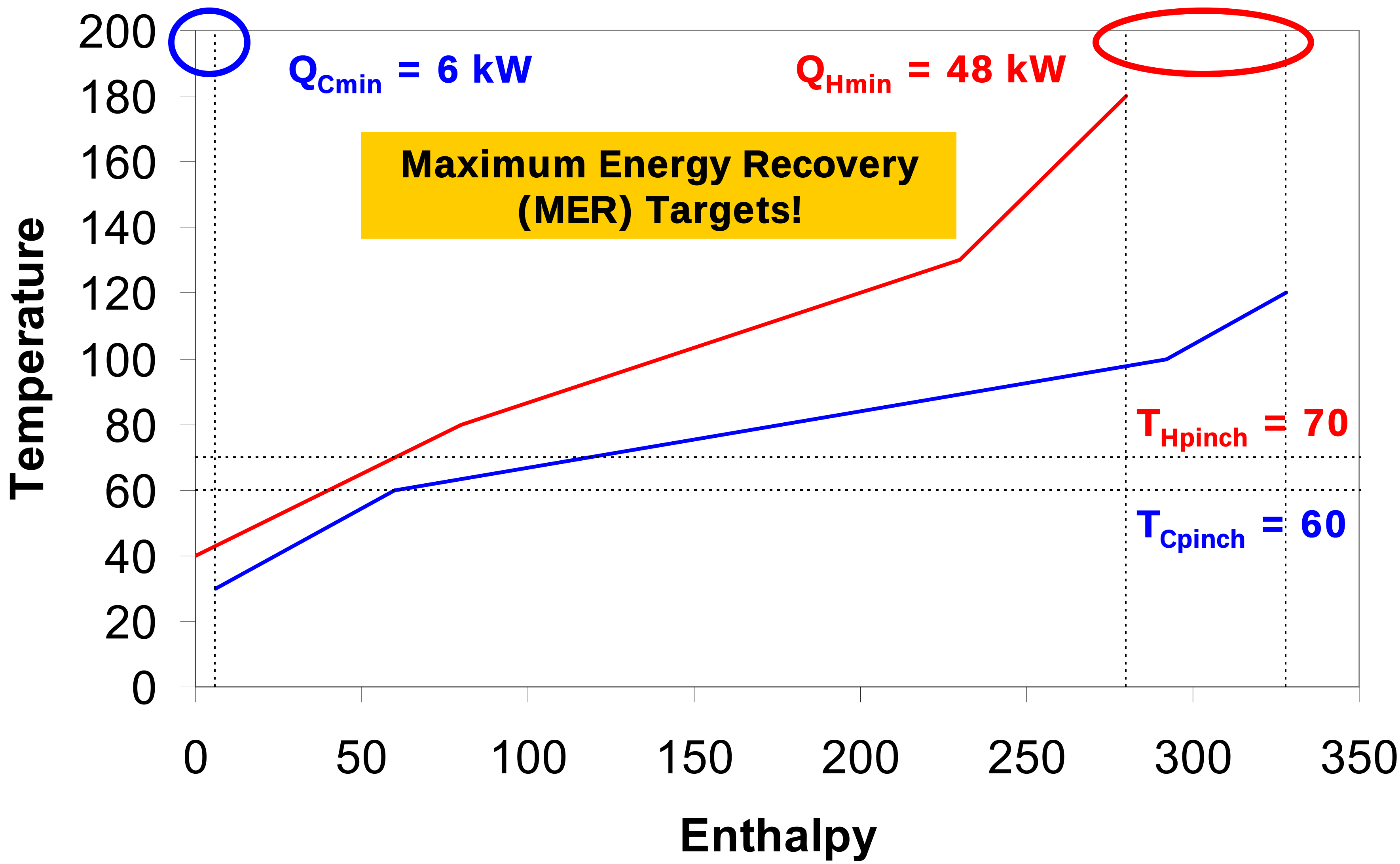




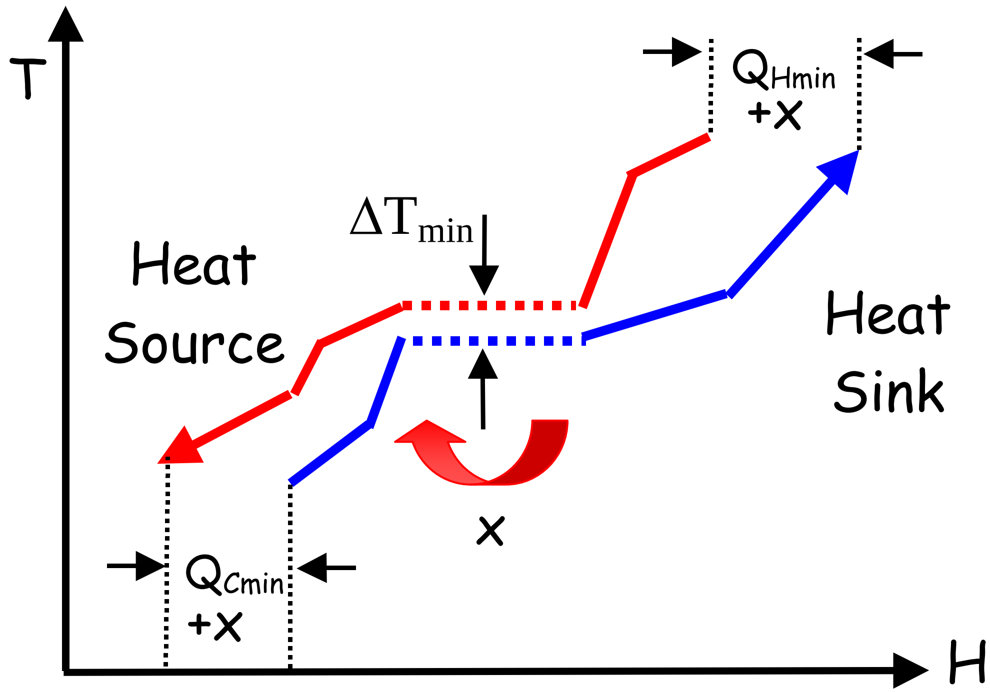
Thermal Pinch Diagram



Simple Ex. - Pinch Diagram



The Pinch



The "pinch" separates the HEN problem into two parts:

Heat sink - above the pinch, where at least Q_{Hmin} utility must be used
Heat source - below the pinch, where at least Q_{Cmin} utility must be used.

Significance of the Pinch

- Do **not** transfer heat across pinch
- Do **not** use **cold** utilities above the pinch
- Do **not** use **hot** utilities below the pinch

Algebraic Targeting Method

- Temperature scales
  - Hot stream temperatures (**T**)
  - Cold stream temperatures (**t**)

- Thermal equilibrium
  - Achieved when T = t

- Inclusion of temperature driving force ΔT_{min}
  - $T = t + \Delta T_{min}$
  - Thus substracting $\mathbf{\Delta T_{min}}$ from the **hot** temperatures will ensure thermal feasibility at all times

Algebraic Targeting Method

- Exchangeable load of the u'th hot stream passing through the z'th temperature interval:

$$Q_{u,z}^{H} = C_u (T_{z-1} - T_z)$$

- Exchangeable capacity of the v'th cold stream passing through the z'th temperature interval:

$$Q_{v,z}^{C} = C_v (t_{z-1} - t_z) = C_v ((T_{z-1} - \Delta T_{\min}) - (T_z - \Delta T_{\min}))$$

$$\Updownarrow$$

$$Q_{v,z}^{C} = C_v (T_{z-1} - T_z)$$

Algebraic Targeting Method

- Collective load of the hot streams passing through the z'th temperature interval is:

$$\Delta H_z^H = \sum_u Q_{u,z}^H$$

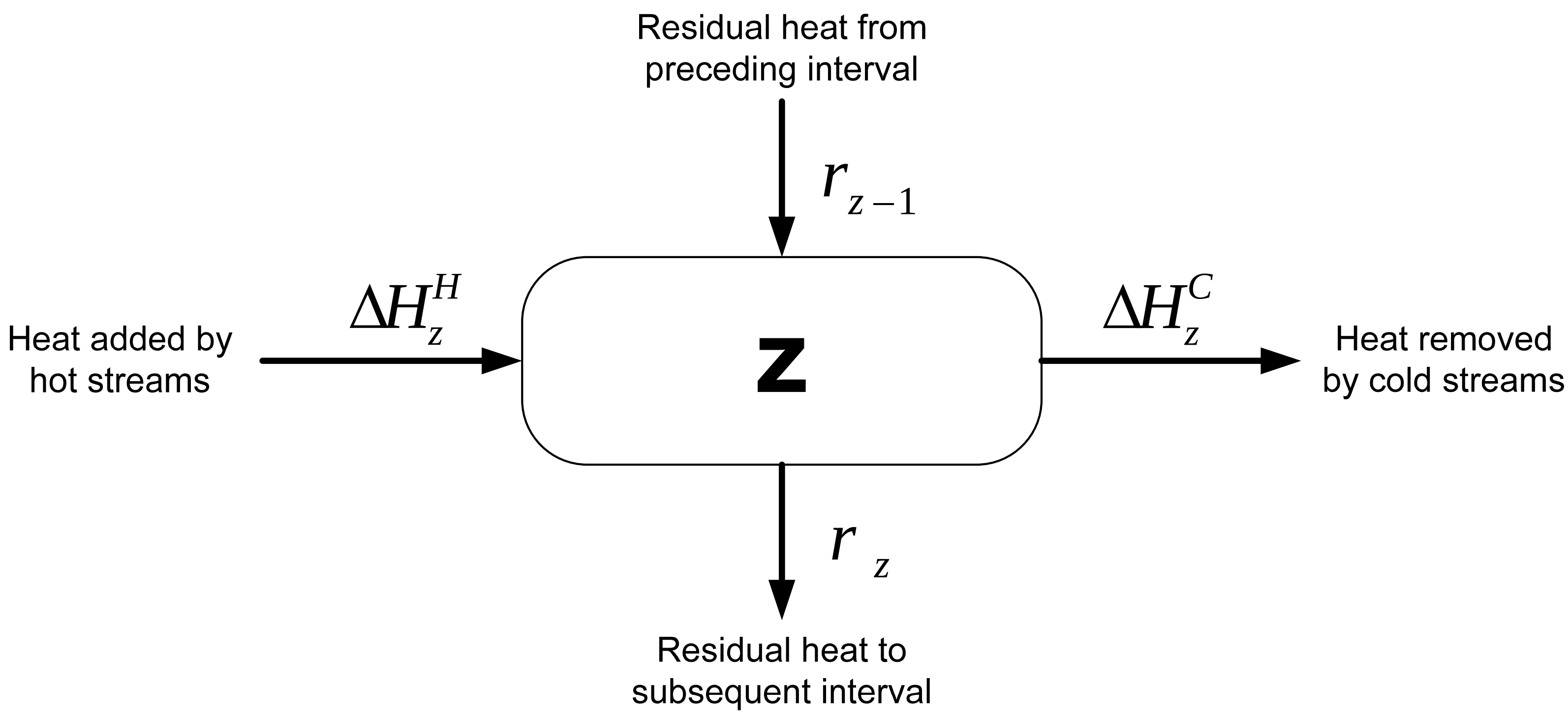
- Collective capacity of the cold streams streams passing through the z'th temperature interval is:

$$\Delta H_z^C = \sum_u Q_{v,z}^C$$

Algebraic Targeting Method

- Heat balance around each temperature interval:

$$r_z = \Delta H_z^H - \Delta H_z^C + r_{z-1}$$



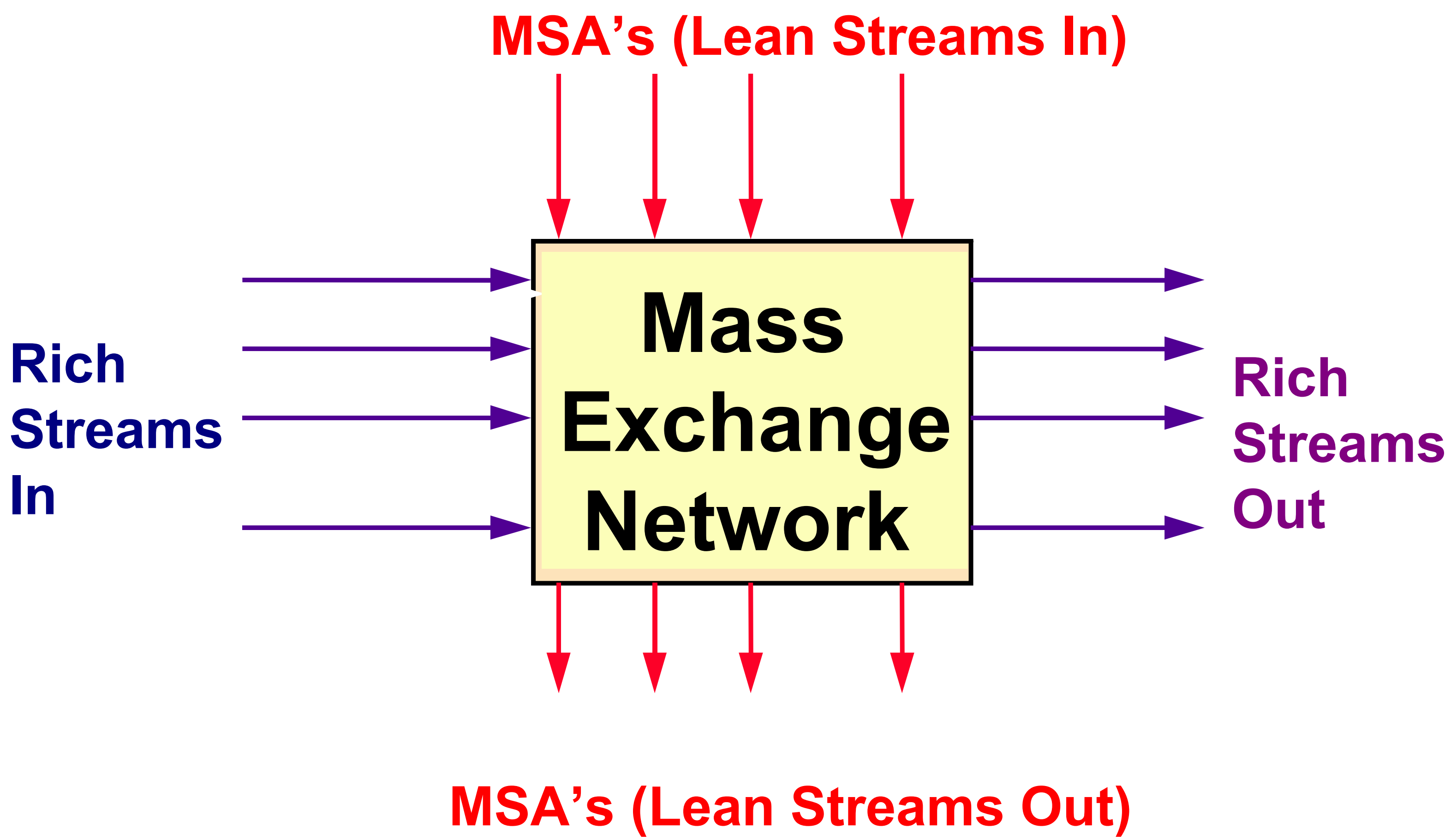
Algebraic Targeting Method

- The enthalpy cascade
  - r_0 is zero (no hot streams exist above the first interval)
  - Feasibility is insured when all the r_z's are **nonnegative**
  - The **most negative** r_z corresponds to the minimum heating utility requirement (**Q_{Hmin}**) of the process
  - By adding an amount (**Q_{Hmin}**) to the top interval a **revised enthalpy cascade** is obtained

Algebraic Targeting Method

- The revised enthalpy cascade
  - On the revised cascade the location of $\mathbf{r_z = 0}$ corresponds to the heat-exchange pinch point
  - Overall energy balance for the network must be realized, thus the residual load leaving the **last temperature interval** is the minimum cooling utility requirement ($\mathbf{Q_{Cmin}}$) of the process

Mass Exchange Networks 1:4



Mass Exchange Networks 2:4

- What do we know?
  - Number of rich streams (N_R)
  - Number of process lean streams or process MSA's (N_{SP})
  - Number of external MSA's (N_{SE})
  - Rich stream data
    - Flowrate (G_i), supply (y_i^s) and target compositions (y_i^t)
  - Lean stream (MSA) data
    - Supply (x_j^s) and target compositions (x_j^t)
    - Flowrate of each MSA is unknown and is determined as to minimize the network cost

Mass Exchange Networks 3:4

- Synthesis Tasks
  - Which mass-exchange operations should be used (e.g., absorption, adsorption, etc.)?
  - Which MSA's should be selected (e.g., which solvents, adsorbents, etc.)?
  - What is the optimal flowrate of each MSA?
  - How should these MSA's be matched with the rich streams (i.e., stream parings)?
  - What is the optimal system configuration?

Mass Exchange Networks 4:4

- Classification of Candidate Lean Streams (MSA's)
  - N_{SP} Process MSA's
  - N_{SE} External MSA's

$N_S = N_{SP} + N_{SE}$

- Process MSA's
  - Already available at plant site
  - Can be used for pollutant removal virtually for free
  - Flowrate is bounded by availability in the plant

- External MSA's
  - Must be purchased from market
  - Flowrates determined according to overall economics

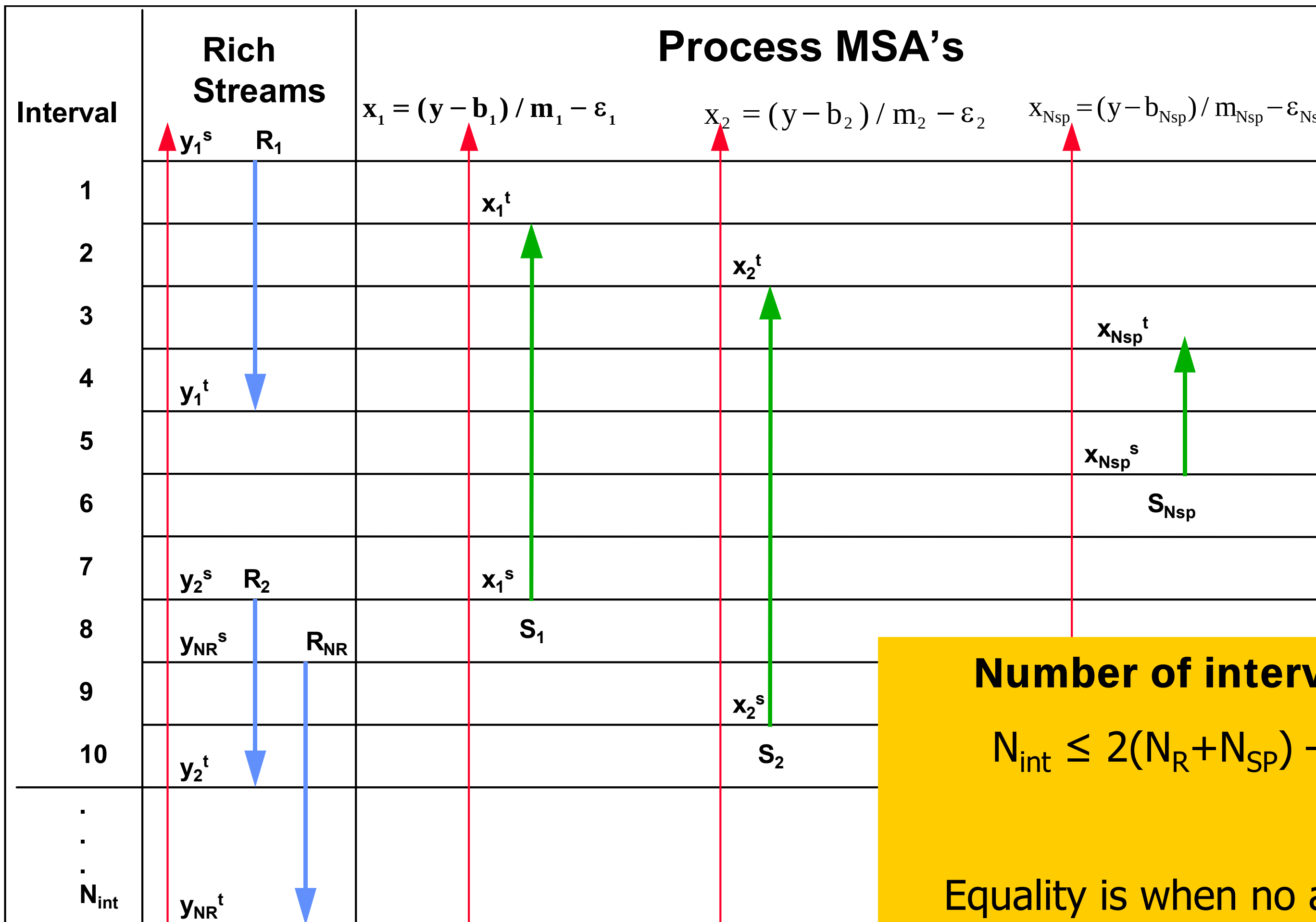
Mass Integration Overview

- Pinch Diagram
  - Useful tool for representing global transfer of mass
  - Identifies performance targets, e.g. MOC
  - Has accuracy problems for problems with wide ranging compositions or many streams

- Algebraic Method
  - No accuracy problems
  - Can handle many streams easily
  - Can be programmed and formulated as optimization problems

Algebraic Mass Integration 1:7

- Composition Interval Diagram (CID)



Number of intervals

$N_{int} \leq 2(N_R + N_{SP}) - 1$

Equality is when no arrow heads or tails coincide!

Algebraic Mass Integration 2:7

- Table of Exchangeable Loads (TEL)
  - Exchangeable load of the *i*'th rich stream passing through the *k*'th interval is:

$$W_{i,k}^{R} = G_i(y_{k-1} - y_k)$$

  - Exchangeable capacity of the *j*'th process MSA which passes through the *k*'th interval is calculated as:

$$W_{j,k}^{S} = L_j^C(x_{j,k-1} - x_{j,k})$$

Algebraic Mass Integration 3:7

- Table of Exchangeable Loads (TEL) (Cont'd)
  - Collective load of the rich streams passing through the *k*th interval is:

$$W_k^R = \sum_{i \text{ passes through interval } k} W_{i,k}^R$$

  - Collective capacity of the lean streams passing through the *k*th interval is:

$$W_k^S = \sum_{j \text{ passes through interval } k} W_{j,k}^S$$

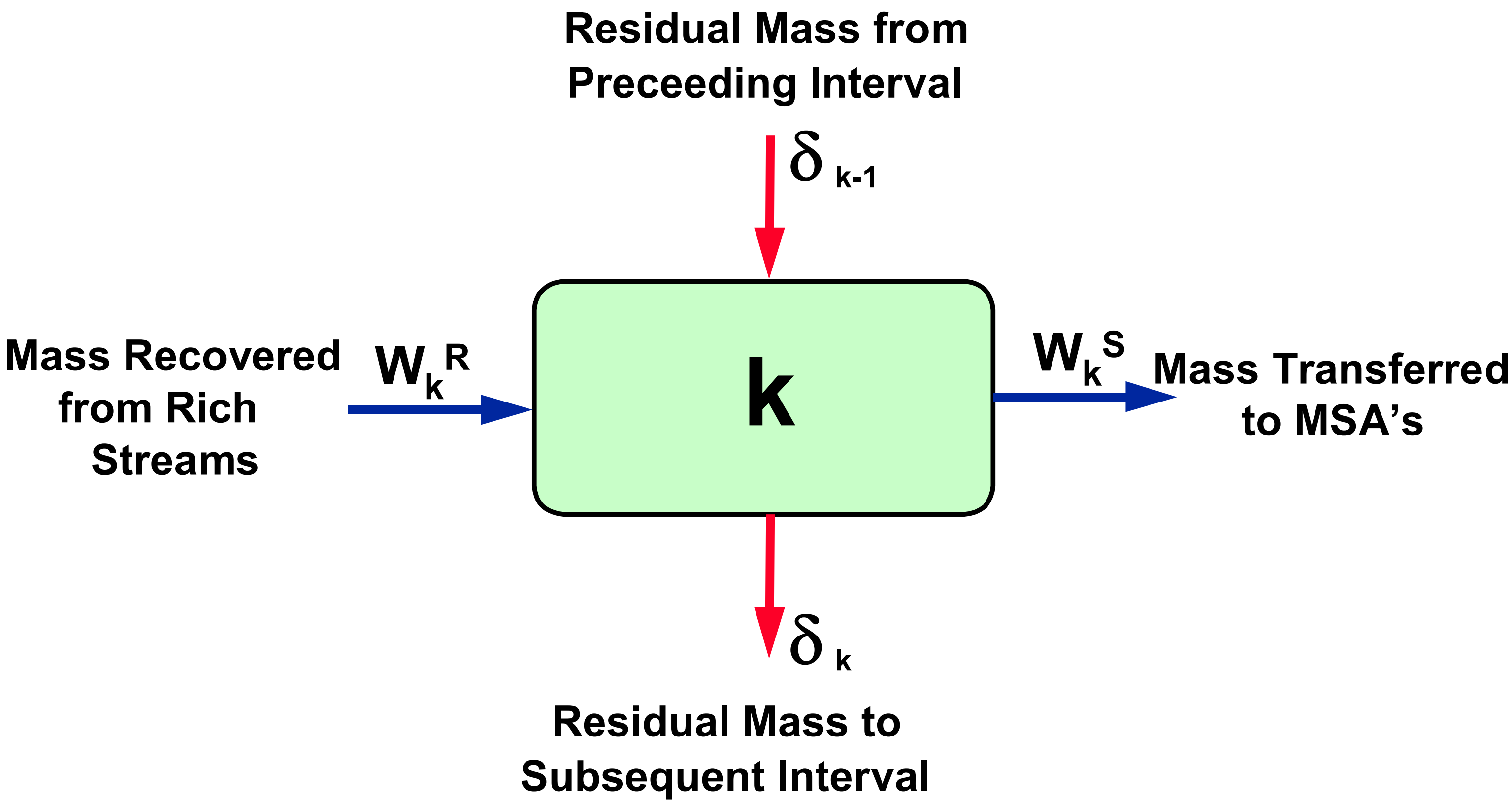
Algebraic Mass Integration 4:7

- Mass Exchange Cascade Diagram
  - Within each composition interval it is possible to transfer a certain mass of pollutant from a rich to a lean stream
  - It is also possible to transfer mass from a rich stream in an interval to a lean stream in **lower** interval
  - Component material balance for interval *k*

$$W_k^R + \delta_{k-1} - W_k^S = \delta_k$$

Algebraic Mass Integration 5:7

- Mass Exchange Cascade Diagram (Cont'd)



Algebraic Mass Integration 6:7

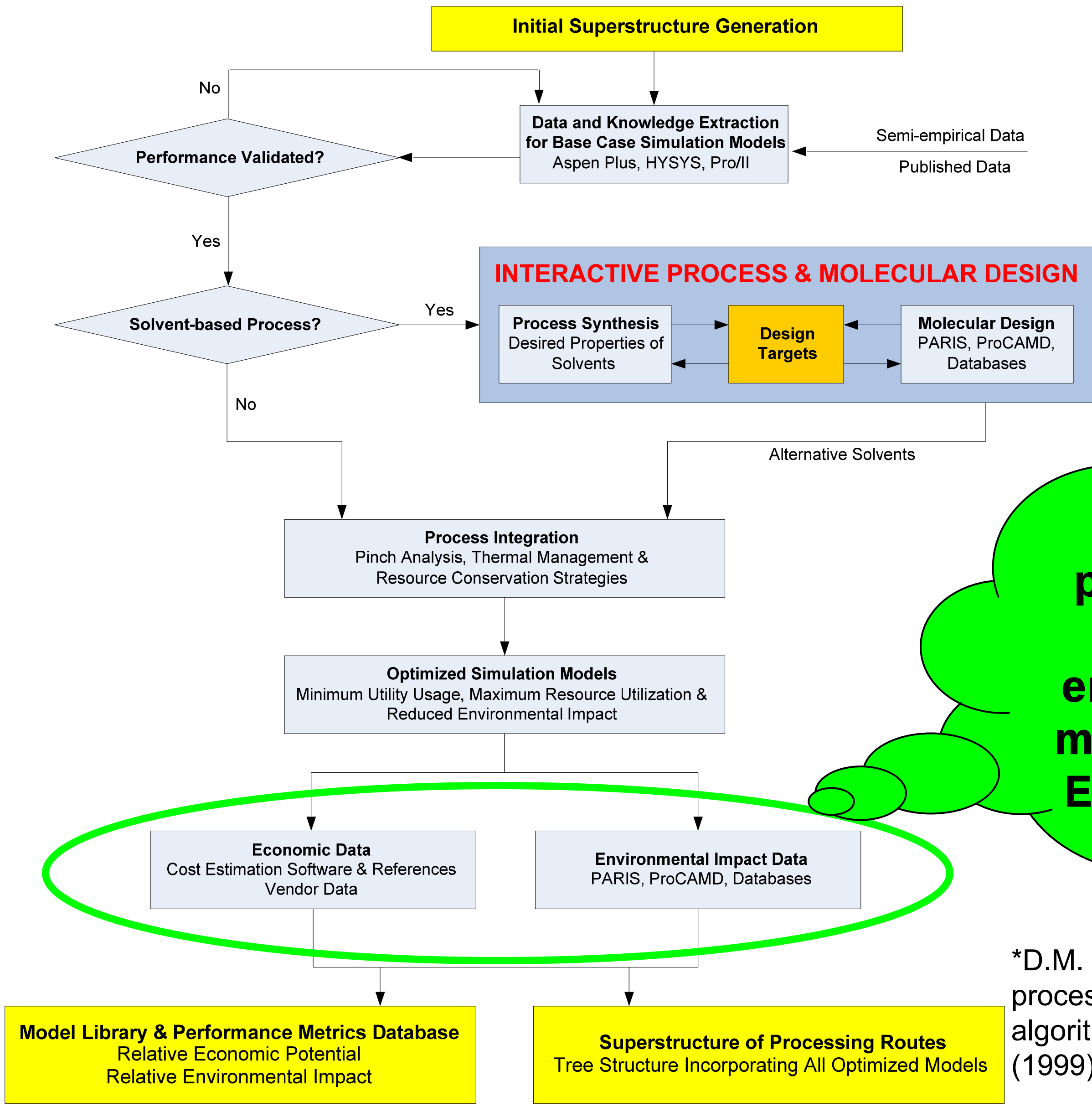
- Comments
  - δ_0 is zero (no rich streams exist above the first interval)
  - Feasibility is insured when all the δ_k's are nonnegative
  - The most negative δ_k corresponds to the excess capacity of the process MSA's in removing the targeted species.
  - After removing the excess capacity of MSA's, one can construct a **revised TEL/cascade diagram** in which the flowrates and/or outlet compositions of the process MSA's have been adjusted.

Algebraic Mass Integration 7:7

- Comments (Continued)
  - On the revised cascade diagram the location of **residual mass = zero** corresponds to the mass-exchange pinch composition.

  - Since an overall material balance for the network must be realized, the **residual mass leaving the lowest composition interval of the revised cascade diagram** must be removed by external MSA's.

Problem Approach 1:2



Obtain economic performance metrics as well as environmental impact metrics through use of EPA WAR algorithm.*

*D.M. Young and H. Cabezas. "Designing sustainable processes with simulation: the waste reduction (WAR) algorithm." Computers and Chemical Engineering 23 (1999).

Economic Data 1:3

- **Choose between two methods of measuring value:**
  - Gross profit (GP) method
    - Measures revenues minus costs over a fixed period of time (basis of profit per hour, day, week, etc.)
    - No need for prediction of future economic conditions
    - Simplicity, ease of use, and reduced computational time
  - Net present value (NPV) method
    - Measures net present value of decisions over a pre-determined period of time (~10-20 years)
    - Takes into account the time value of money, current and anticipated subsidy and incentive programs, and depreciation
    - Robust, with improved ability to quantify added value

Economic Data 2:3

- **Economic data needed for GP method**
  - Fixed cost
    - List equipment necessary for integrated process
    - Determine total equipment cost for a number of capacities
    - Develop a function (may be nonlinear) for total fixed cost as a function of capacity
    - Assume straight line amortization to determine annualized fixed cost as function of capacity and divide by proper factors for fixed cost per time per product flow
  - Variable cost
    - Use established methodology (e.g. Peters & Timmerhaus) to determine how variable costs are calculated
    - Add total variable costs (may be function of capacity if variable cost is based capital investment)
    - Divide by proper factor for variable cost per output basis

Economic Data 3:3

- **Economic data needed for NPV method**
  - In addition to data needed for GP method:
    - Window of time over which to calculate NPV
    - Estimated marginal tax rate at which decisions are taking place
    - Information on current and future tax credits and deductions, subsidies, etc. for possible products or pathways
    - Probabilities on legislative courses of action which will impact the economics of products or pathways
    - Time value of money interest rate
    - Acceptable depreciation method (MACRS vs. straight-line)
    - Depreciation schedules for specific equipment items, which may vary
    - Monies dedicated to hedging against unfavorable market action (e.g. options, futures, derivatives)

Environmental Data 1:2

- **First, determine method used to measure environmental impact**
  - US-EPA Waste Reduction (WAR) Algorithm
  - The impact of chemical k in terms of potential environmental impact per mass is[2]:

$$\Psi_k = \sum_l a_l \psi_{kl}^s$$

Where a_l is a weighting factor between 0 and 10 and ψ_{kl}^s is a normalized score on scale l:

$$\psi_{kl}^s = \frac{(score)_{kl}}{< (score)_k >_l}$$

[2]D.M. Young and H. Cabezas. "Designing sustainable processes with simulation: the waste reduction (WAR) algorithm." Computers and Chemical Engineering 23 (1999).

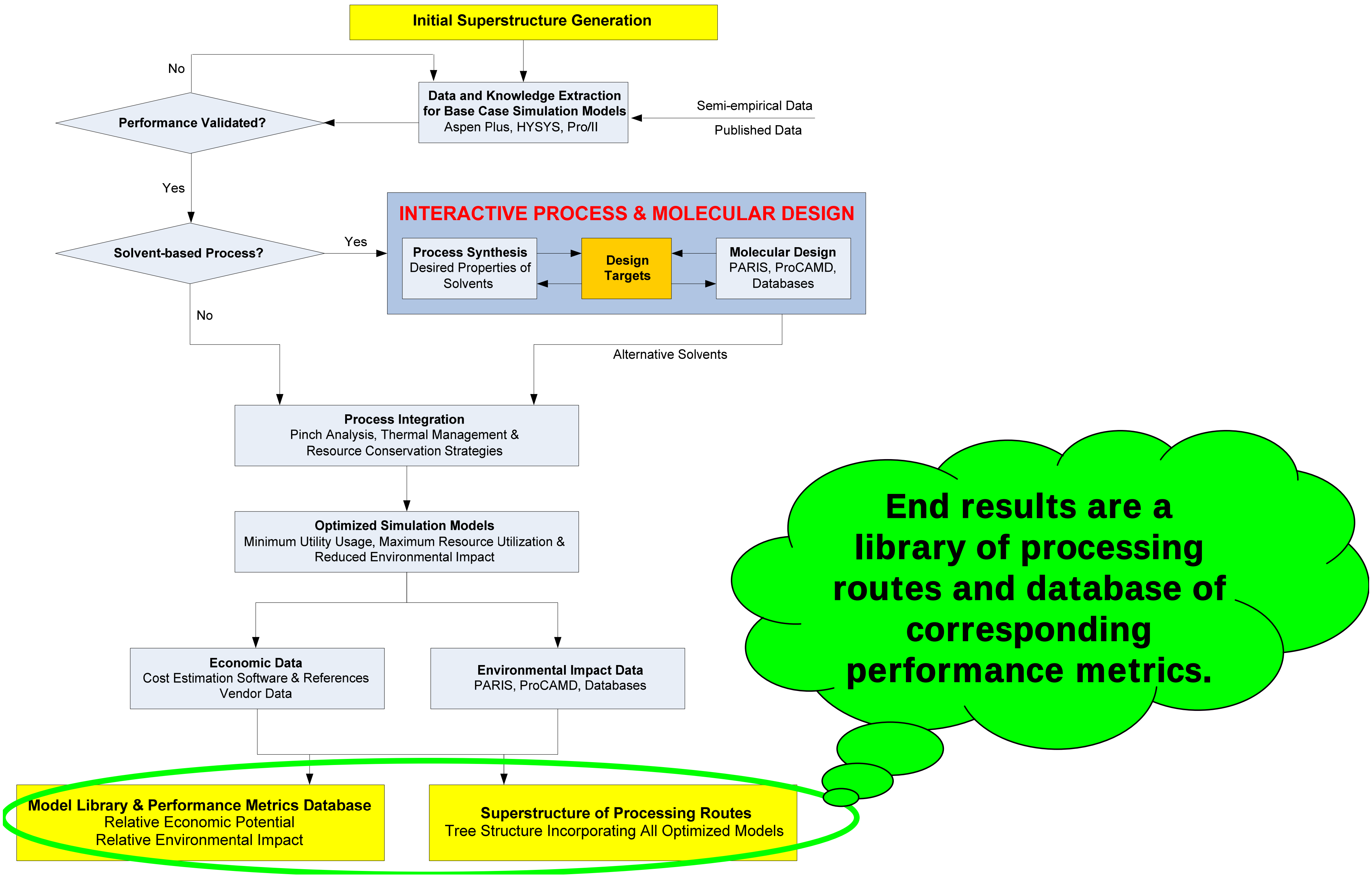
Environmental Data 2:2

- **Next, look at individual criteria to be measured to determine what data is needed**
  - US-EPA Waste Reduction (WAR) Algorithm
  - Impact calculated by WAR Algorithm based on eight criteria:

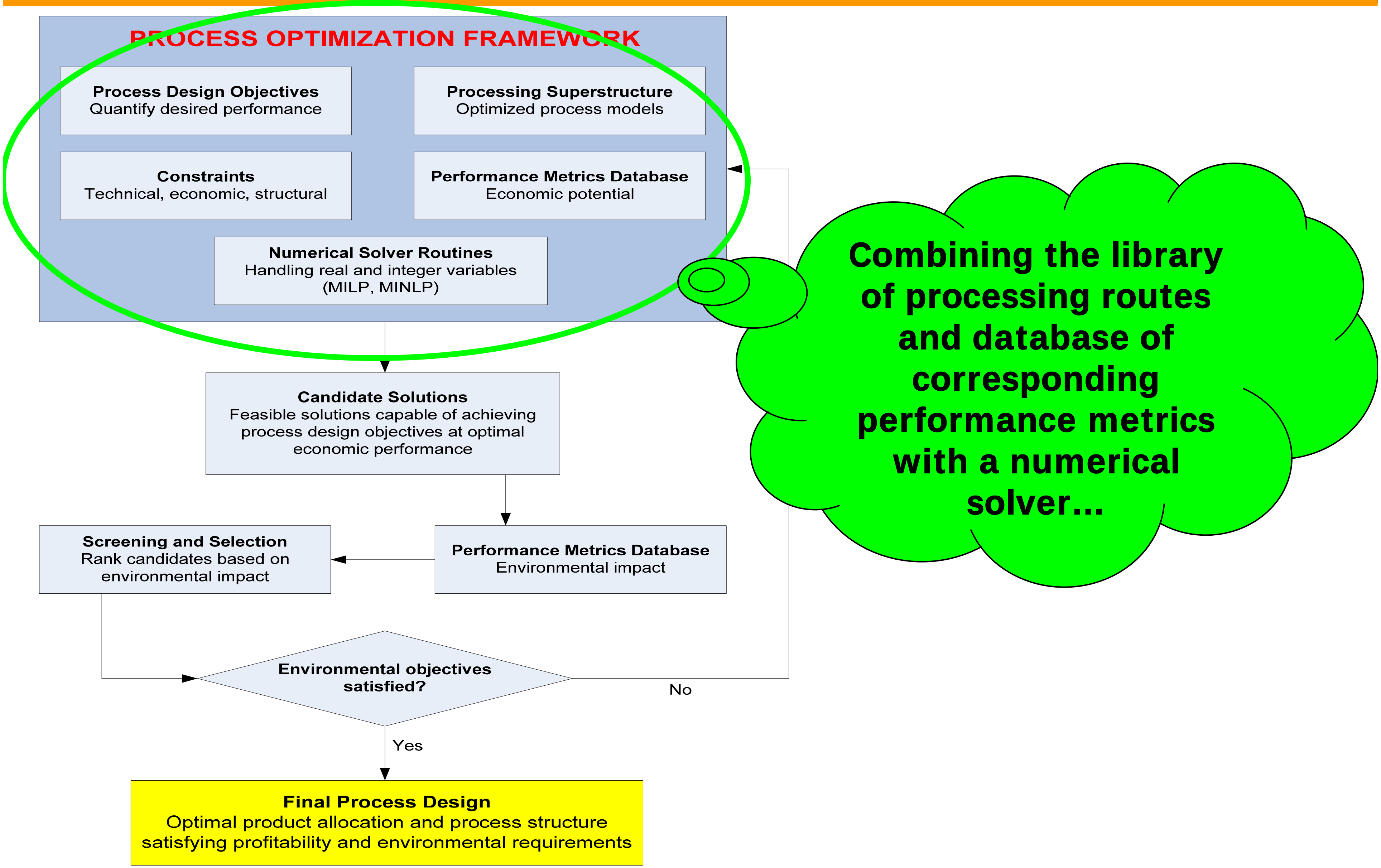
Global warming	Human toxicity by ingestion
Ozone depletion	Human toxicity by inhalation or dermal exposure
Acidification	Aquatic toxicity
Photochemical oxidation	Terrestrial toxicity

  - Gather data from integrated models in order to determine scores
  - Use of software and databases may decrease difficulty of determining environmental impact

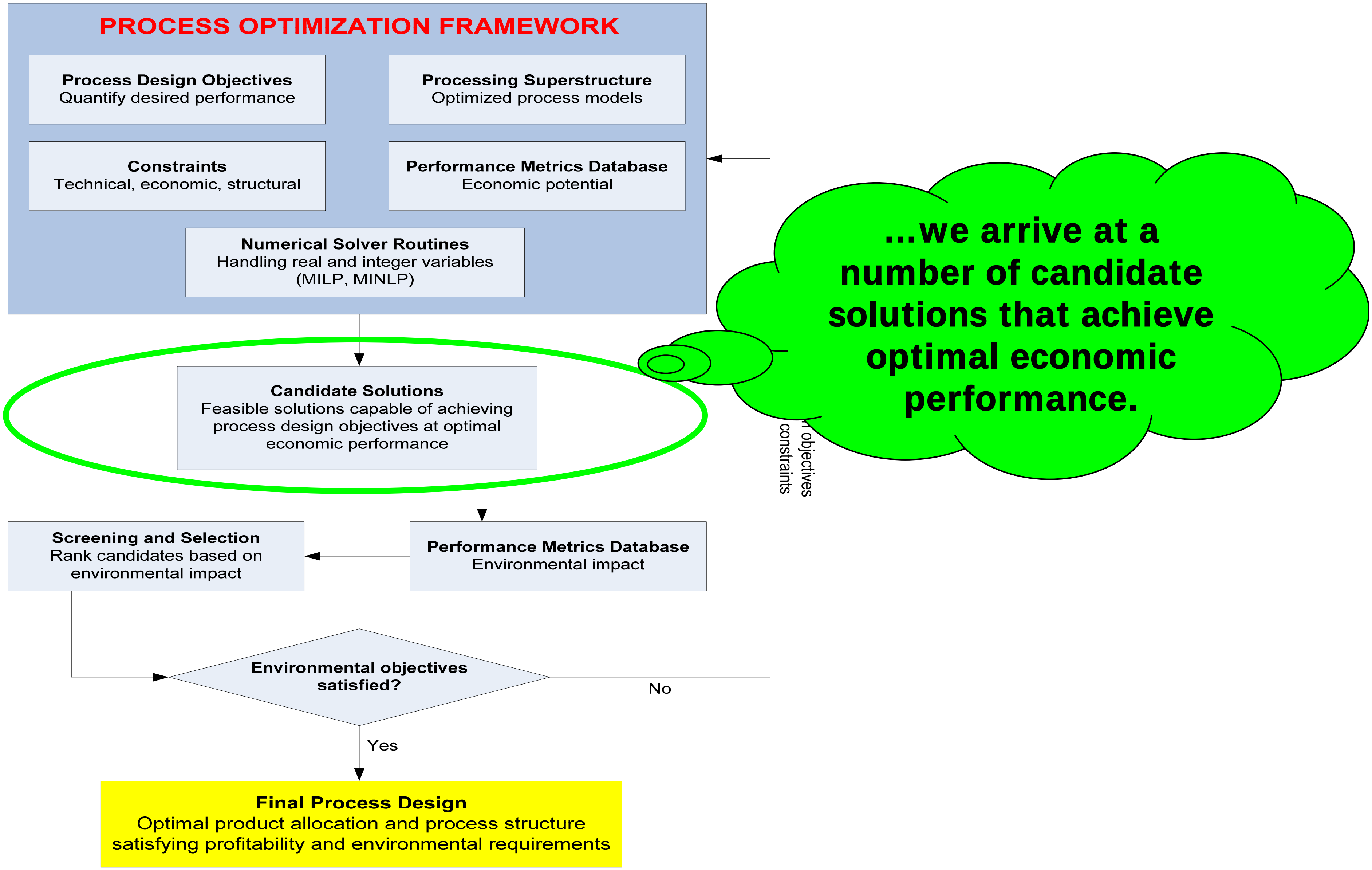
Problem Approach 1:2



Problem Approach 2:2



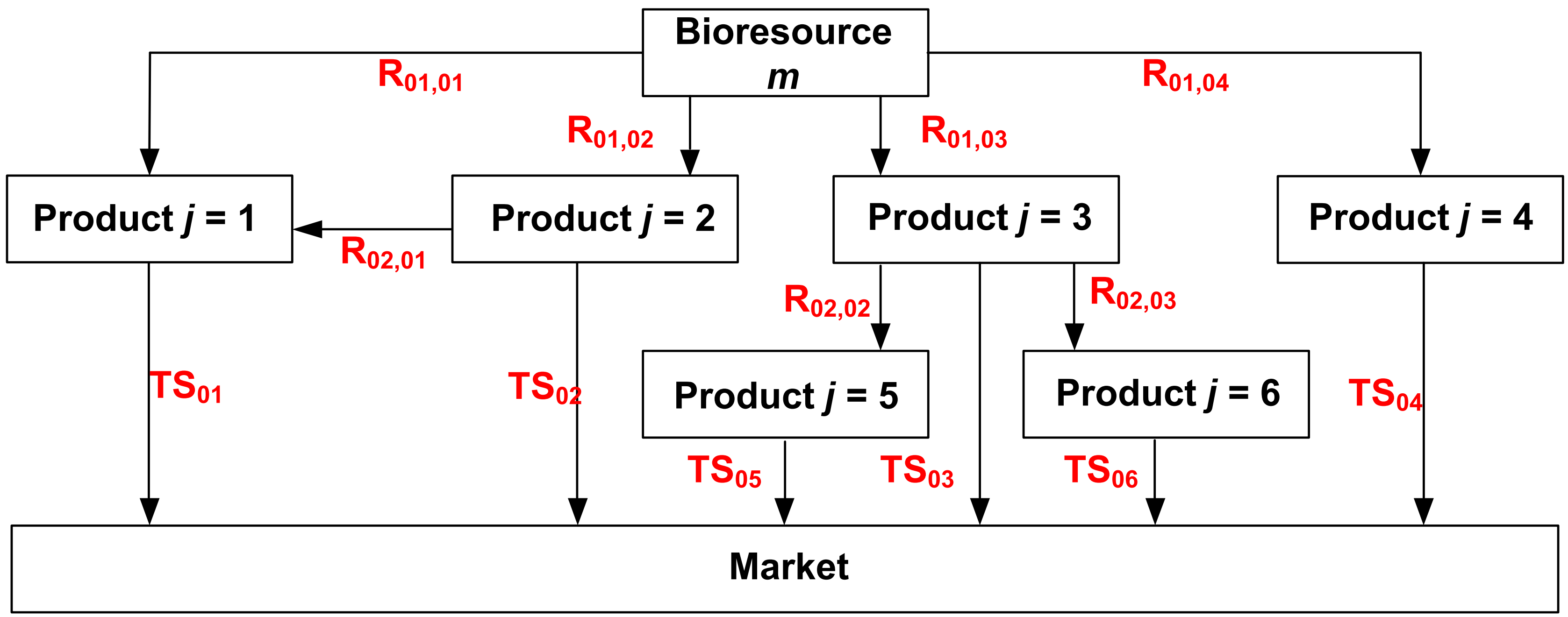
Problem Approach 2:2



General Model 1:1

Pathways denoted by $R_{i,j}$ or TS_k

- *R* internal production pathway
- *TS* pathway to market
- *i* number of processing steps away from raw material
- *j* pathway at specified level i
- *k* product sold on the market



Economic Optimization 1:4

- **Gross profit method**

$$\max \boldsymbol{Profit} = \sum_{m}\left(\sum_{k} TS_k C_k^s - \sum_{i}\sum_{j} R_{mij} C_{mij}^P - C_m^{BM} \sum_{j} R_{m1j}\right)$$

- **TS_k** Amount of product *k* sold on the market
- **C_k^s** Sales price of product *k*
- **R_{mij}** Processing rate of route *mij*
- **C_{mij}^P** Processing cost (fixed + variable) of route *mij* per unit output
- **R_{m1j}** Processing rate of bioresource *m* through route *1j*
- **C_m^{BM}** Purchase price of bioresource *m*

Economic Optimization 2:4

- **Net present value method**

$$\max NPV = \sum_t \left[\frac{GP_t(1 - Tax_t) + Dep_t Tax_t - Hedge_t + Gov_t}{(1 + TVM)^t} \right]$$

$$\mathrm{GP_t} = \sum_m \left(\sum_k TS_{kt} C^S_{kt} - \sum_i \sum_j R_{mijt} C^P_{mijt} - C^{BM}_{mt} \sum_j R_{m1jt} \right)$$

- **$\mathbf{Tax_t}$** Marginal taxation rate in year *t*
- **$\mathbf{Dep_t}$** Depreciation amount in year *t*
- **$\mathbf{Hedge_t}$** Expenses (revenues) of hedging in year *t*
- **$\mathbf{Gov_t}$** Government incentives (penalties) in year t
- **TVM** Time value of money (market rate of return)

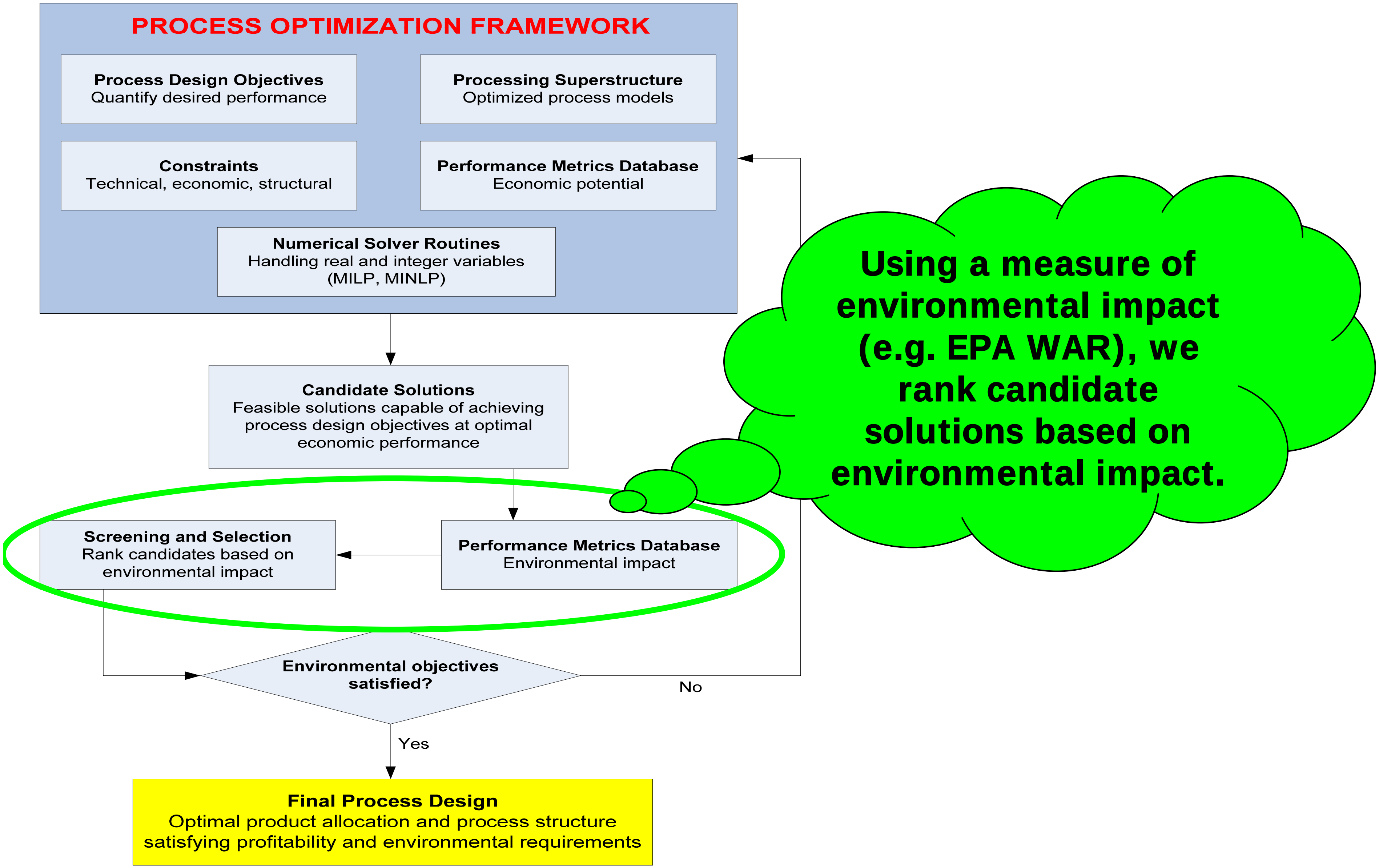
Economic Optimization 3:4

- **Constraints**
  - Total capital investment, which dictates capacity
    - Alternatively, maximum feasible capacity
  - Maximum flowthrough based on capacity
  - Mass balances around the product points
    - In * Conversion factor = To Sell + To Process + Waste
  - Output composition
  - Energy balances
  - Biomass availability
  - Maximum output based on market and supply chain conditions
  - Separations (purity, energy usage, size)

Economic Optimization 4:4

- **Generate list of candidate solutions**
  - Once the "best answer" is found, enter a constraint which makes this "best answer" infeasible for future optimization runs
  - Keep track of process configurations, product distributions, and objective values of gross profit/NPV of each optimization run
  - Determine a termination point (e.g. once objective function dips below percentage of the first "best answer")

Problem Approach 2:2



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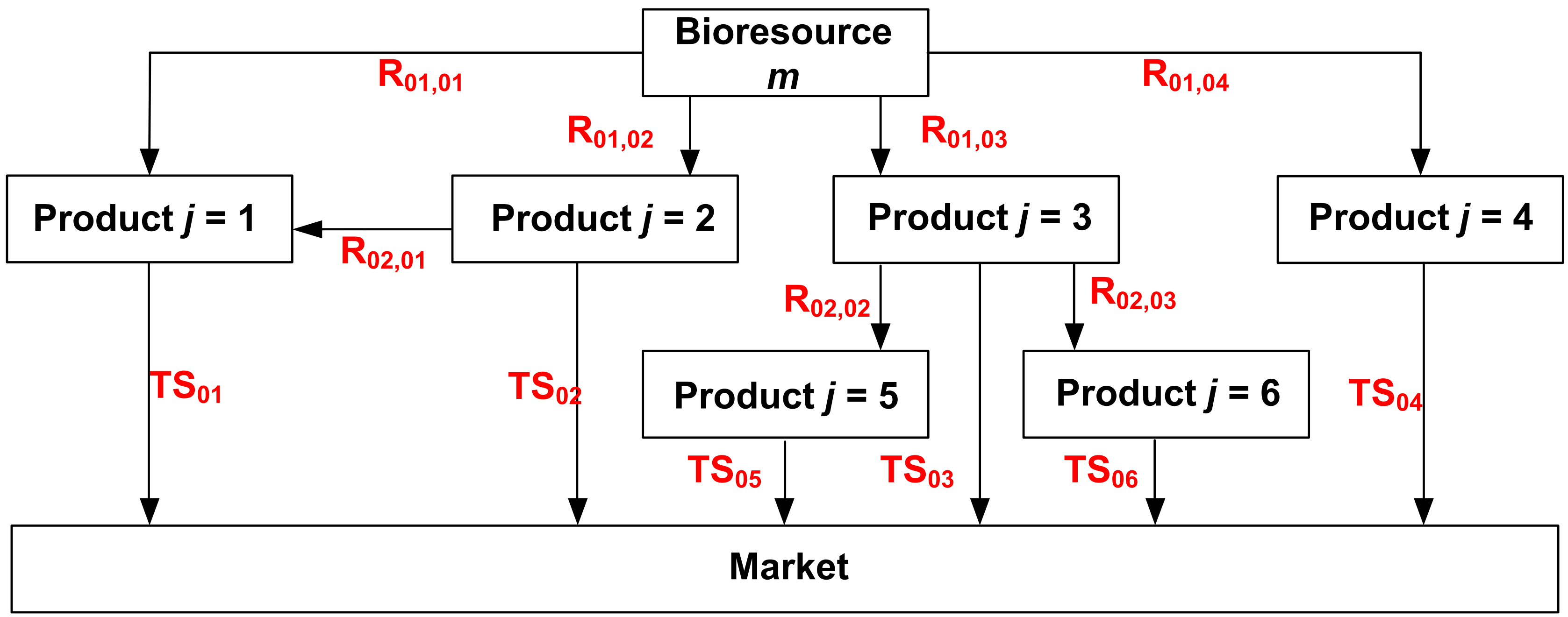
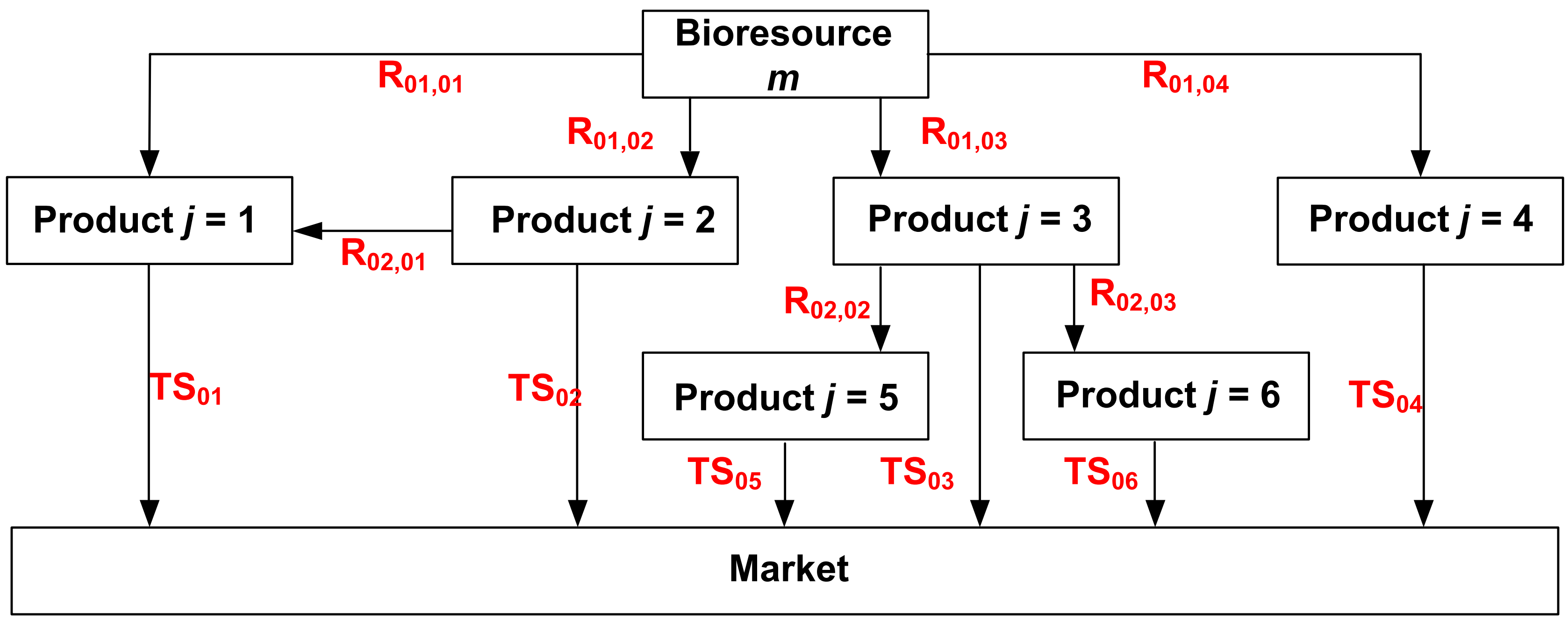
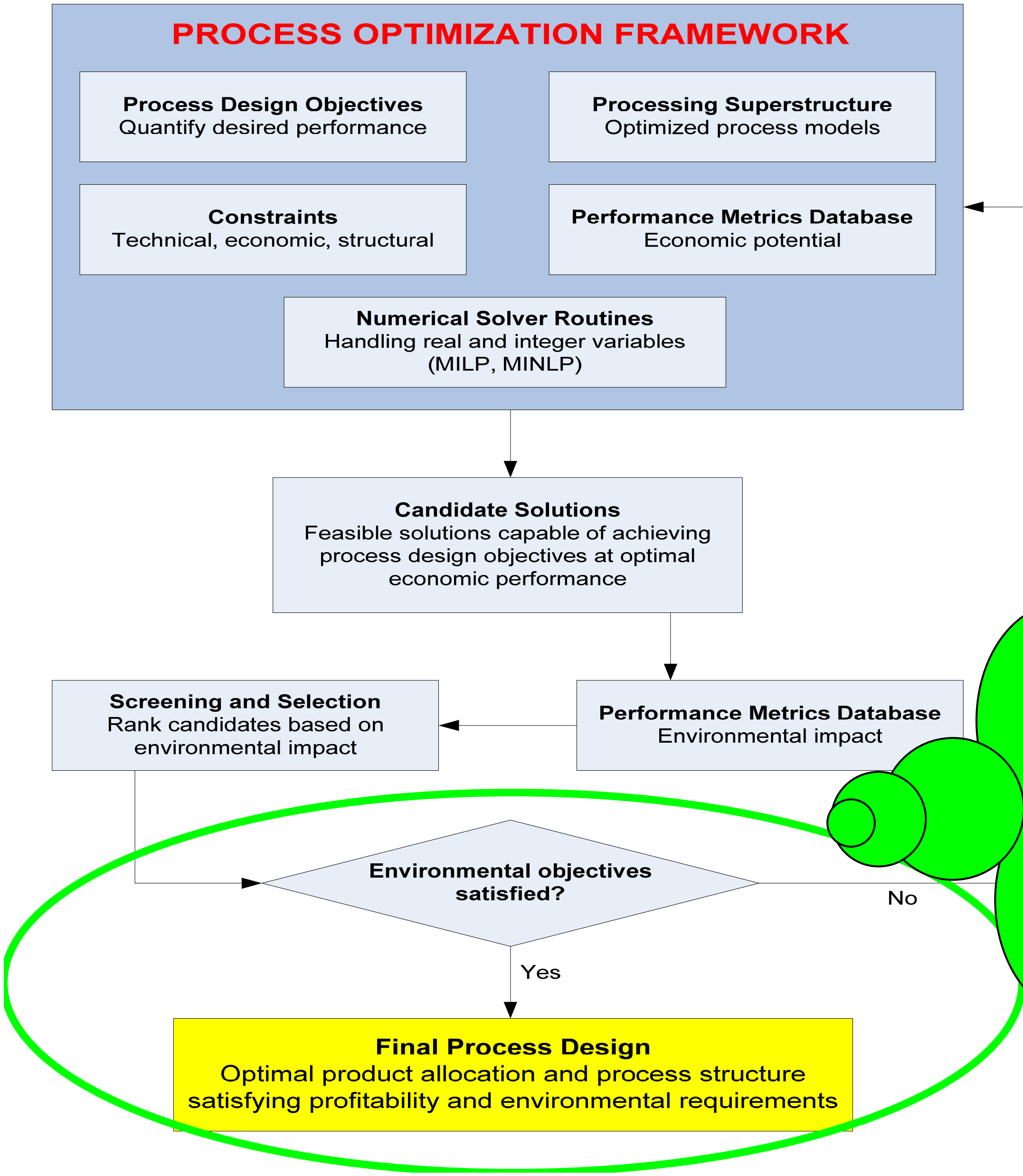


Ranking Example 1:1

Active Pathways	Product Distribution	NPV	WAR Score
$R_{01,01}$-TS_{01}	1 only	$10.7M	40
$R_{01,02}$-$R_{02,01}$-TS_{01}	1 only	$9.8M	42
$R_{01,02}$-TS_{02}	2 only	$9.4M	37
$R_{01,03}$ split to $R_{02,02}$-TS_{05} and TS_{03}	5 and 3	$9.1M	46
$R_{01,04}$-TS_{04}	4 only	$8.2M	28



Problem Approach 2:2

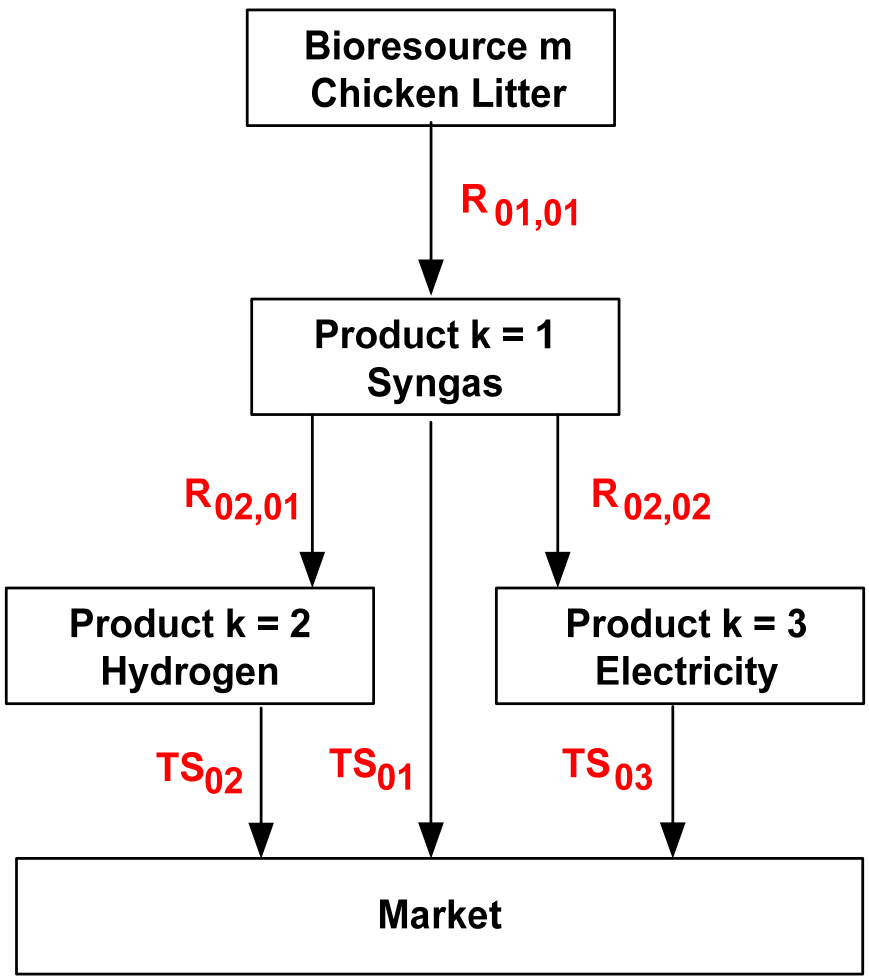


If environmental objectives are satisfied, then we have arrived at the final process design.

This methodology decouples the issues of economic and environmental performance.

Chicken Litter Example 1:6

- **Case study: Chicken litter biorefinery**



- Chicken litter may be gasified and sold to supply chain partners via pipeline, sold as hydrogen after water gas shift and cleanup, or used to produce electricity
- For simplicity, environmental impact, solvent replacement, and process integration are omitted in order to focus on problem formulation and optimization

Chicken Litter Example 2:6

- **Use gross profit method for simplicity**

$$\max Profit = \sum_m \left(\sum_k TS_k C_k^S - \sum_i \sum_j R_{mij} C_{mij}^P - C_m^{BM} \sum_j R_{m1j} \right)$$

  - TS_k Amount of product *k* sold on the market
  - C_k^s Sales price of product *k*
  - R_{mij} Processing rate of route *mij*
  - C_{mij}^P Processing cost (fixed + variable) of route *mij* per unit output
  - R_{m1j} Processing rate of bioresource *m* through route *1j* (maximum biomass constraint)
  - C_m^{BM} Purchase price of bioresource *m*

- **First, determine scalars C_k^s, C_{mij}^P, and C_m^{BM}**

Chicken Litter Example 3:6

- **List equipment in order to determine fixed cost:**

Chicken Litter to Syngas Equipment	Cost (2005 $K)
Air Separation Unit	52933
Biomass Dryer	32523
Biomass Gasifier & Tar Cracker	18320
Biomass Syngas Cooler and Filter	4998
Biomass Syngas expander	2661
Feedstock Storage Area	867
Total Fixed Cost (2005 $)	$112,302,000

Syngas to Electricity Equipment	Cost (2005 $K)
Combined Cycle Power Island (details omitted)	100091
Total Fixed Cost	$100,091,000

Syngas to Hydrogen Equipment	Cost (2005 $K)
Syngas to H2 (details omitted)	461527
Total Fixed Cost	$461,527,000

- **Sum up variable cost factors:**

Litter to Syngas Cost Category	Cost (2005 $)
Utilities	$96,541
Operating Labor	$98,162
Operating Supervision	$14,724
Maintenance	$10,107,180
Operating Supplies	$1,516,077
Laboratory Charges	$14,724
Overhead	$1,361,771
Administrative	$408,531
Total Variable Cost	$13,617,710.99

Syngas to Hydrogen Cost Category	Cost (2005 $)
Utilities	$127,943,849.88
Operating Labor	$98,162
Operating Supervision	$14,724
Maintenance	$41,537,405
Operating Supplies	$6,230,611
Laboratory Charges	$14,724
Overhead	$20,211,434
Administrative	$6,063,430
Total Variable Cost	$202,114,340

Syngas to Electricity Cost Category	Cost (2005 $K)
Electricity Purchases	$5,893,707.90
Operation and Maintanance	$9,407,549.48
Total Variable Cost	$15,301,257.39

Chicken Litter Example 4:6

- **Add annualized fixed costs to variable costs to get C_{mij}^{P}:**

	Biomass to Syngas	Syngas to Electicity	Syngas to Hydrogen
Total Fixed Cost	$112,302,000	$100,091,000	$461,527,000
Annualized Fixed Cost @ 8% interest over 25 years	$10,401,000	$9,270,000	$42,745,000
Total Variable Costs	$13,618,000	$15,301,000	$202,114,000
Total Annual Product Costs	$24,019,000	$24,571,000	$244,859,000
Annual Output	$4.018*10^{8}$ kg	$1.065*10^{6}$ MWe	$8957*10^{8}$ m^3
Cost per Output	$0.0598/kg	$23.07/MWe	$0.273/$m^3$

- **Find market prices for feedstock (C_m^{BM}) and products (C_k^{s}):**

	Market Price
Chicken litter feedstock	$0.010/kg
Syngas	$0.214/kg
Electricity	$53.370/MWe
Hydrogen	$0.220/$m^3$

- **Perform optimization to determine products sold TS_k and processing pathway amounts R_{mij}**

Chicken Litter Example 5:6

- From process models, determine conversion factors for process points in terms of conversion per unit input:

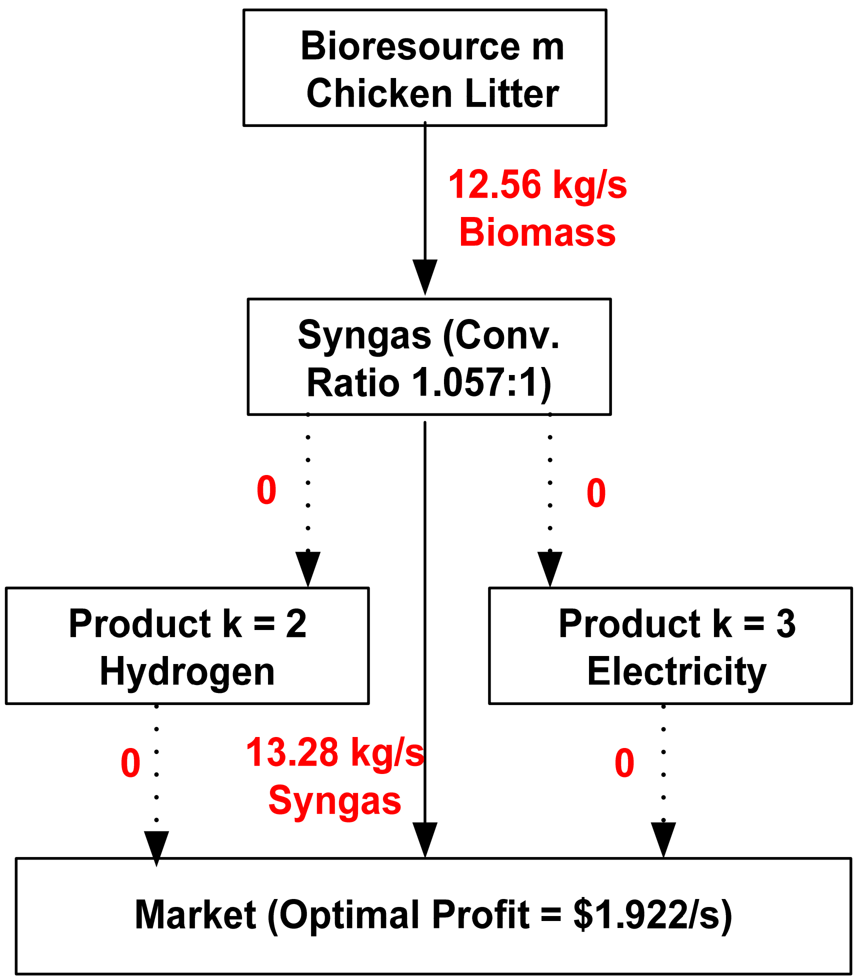
Process	Units	Factor
Chicken litter to syngas	kg/s syngas per kg/s CL	1.057
Syngas to hydrogen	m^3/s hydrogen per kg/s syngas	2.229
Syngas to electricity	MWe/s per kg/s syngas	2.651E-03

- Determine maximum amount of biomass available. In this case, that amount is 12.56 kg/s

- Perform optimization to determine products sold TS_k and processing pathway amounts R_{mij}. Example in GAMS:

Chicken Litter Example 6:6

- **Case study: Chicken litter biorefinery**



  - Using estimated market prices and calculated production rates and costs from simulation models, framework was executed for a proposed chicken litter biorefinery.
  - From observation, syngas should be produced and sold directly to market, and framework confirmed this result.

Future Direction 1:1

– Continue increasing number of simulation models to generate processing costs, production rates, and data for environmental impact metrics

– Develop qualitative predictive models for capital investment as a function of processing rates

– Expand superstructures to include additional products and processes

– Enhance robustness of framework
  – Optimization under uncertainty
  – Alternative formulation methods

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  - Masada Resource Group, LLC
  - Auburn Pulp and Paper Foundation
  - PureVision Technologies
  - Gas Technology Institute (GTI)

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