DESIGN OF INTEGRATED BIOREFINERIES AND BIOENERGY NETWORKS

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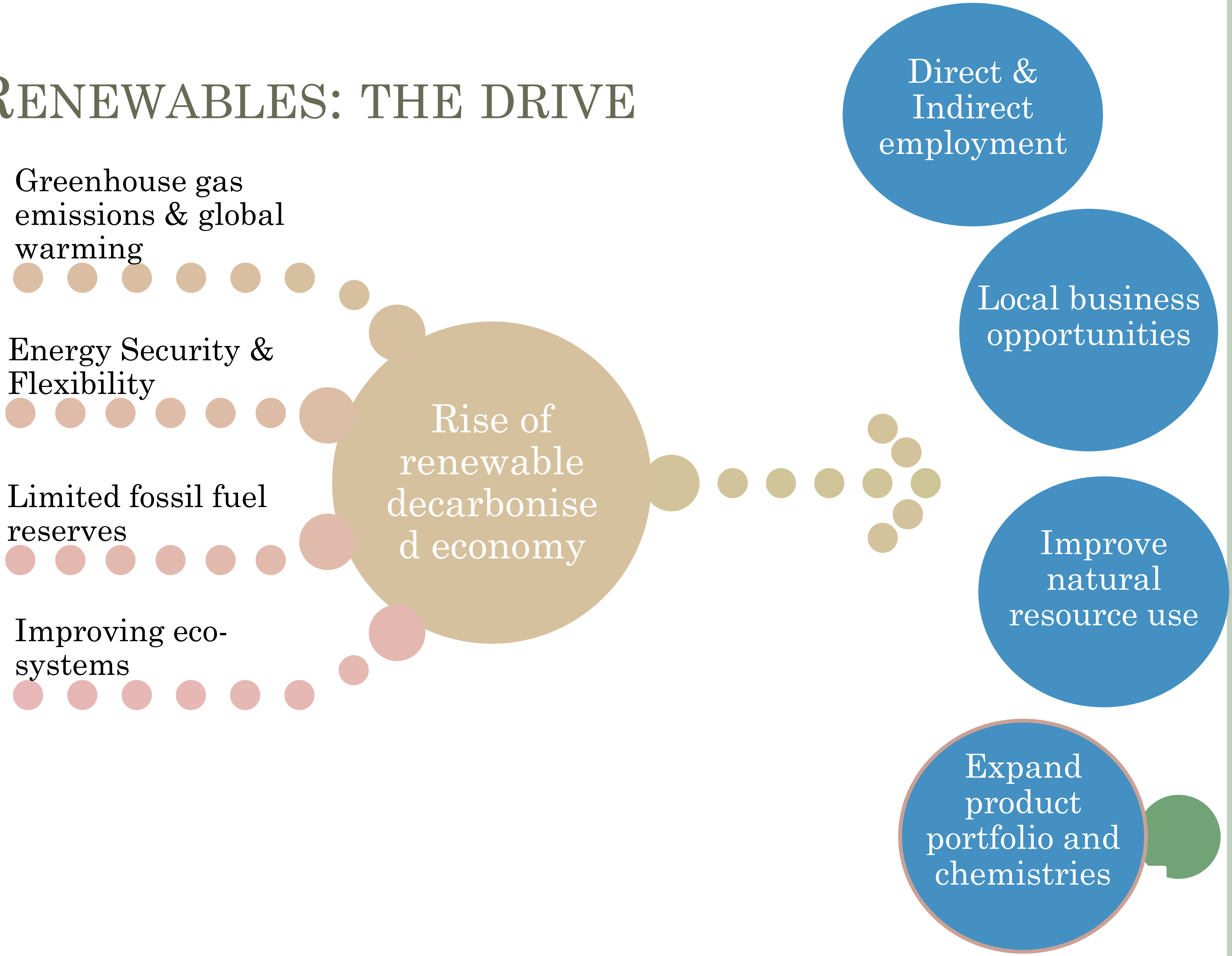
NTUA

- The oldest technical institution (1837) and the first choice of students in science and engineering
- 9 academic schools: 8 on engineering and 1 on applied science
- 8.500 undergraduates and 1.500 postgraduates
- 600 academic staff, 140 scientific
- PG student exporter: numerous graduates continue their careers abroad, regularly at ChE departments and Schools

OUTLINE

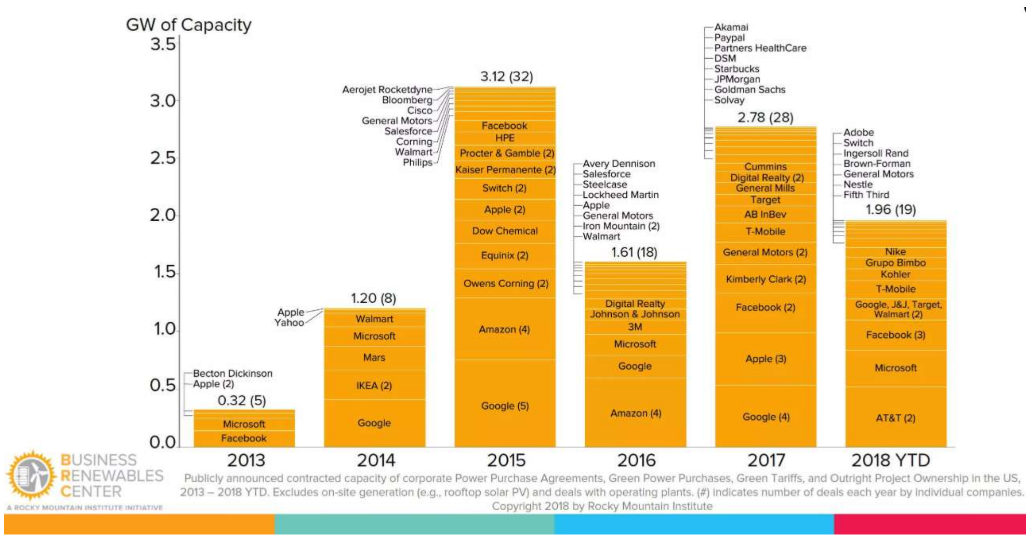
- Business, environmental and social issues behind renewables
- An integrated systems approach
  - Synthesis and screening of chemistries
  - Building process efficiencies and process intensification
  - Cross-sectorial integration, high-throughput search
- Industrial applications in
  - Design of 2G plants and value chains
  - Algae and waste-based refineries
  - Integration with social and urban networks
- Future challenges

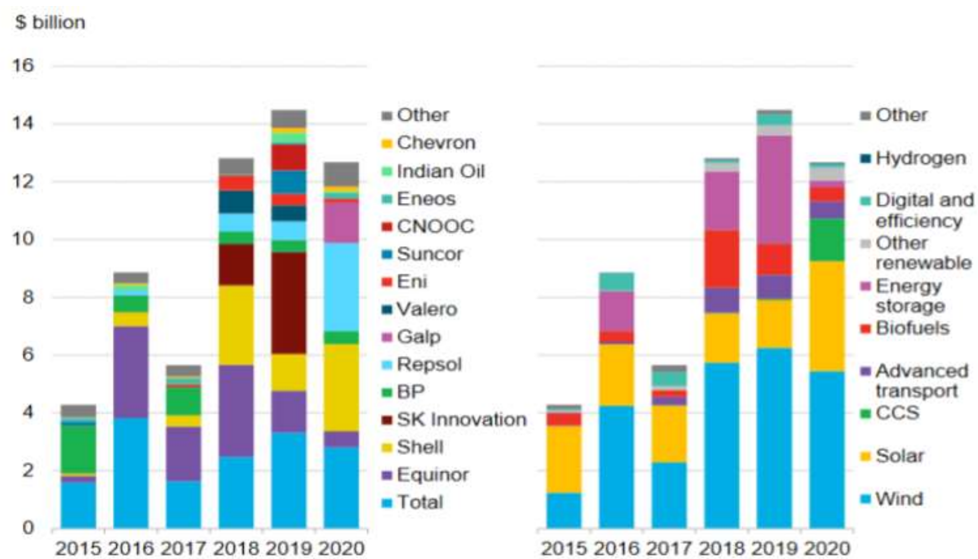
Renewables: the drive



Renewables: the business

- Leading companies investing in renewables - bioenergy



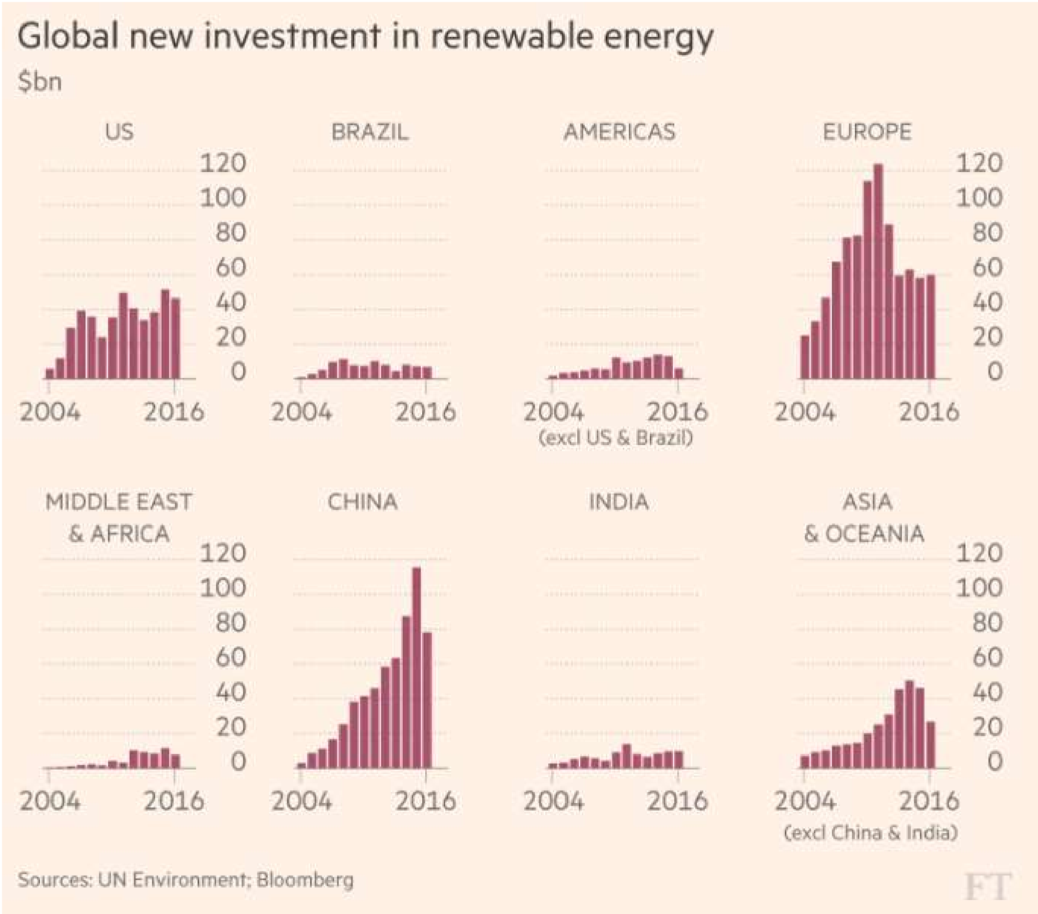


- Companies well beyond the narrow scope of process industries
- Investments relate to: hydrogen, energy storage, biofuels, solar, wind but also
- digital and efficiency, smart applications, business intelligence

https://www.cnet.com/news/renewable-energy-solar-wind-lures-us-big-businesses/

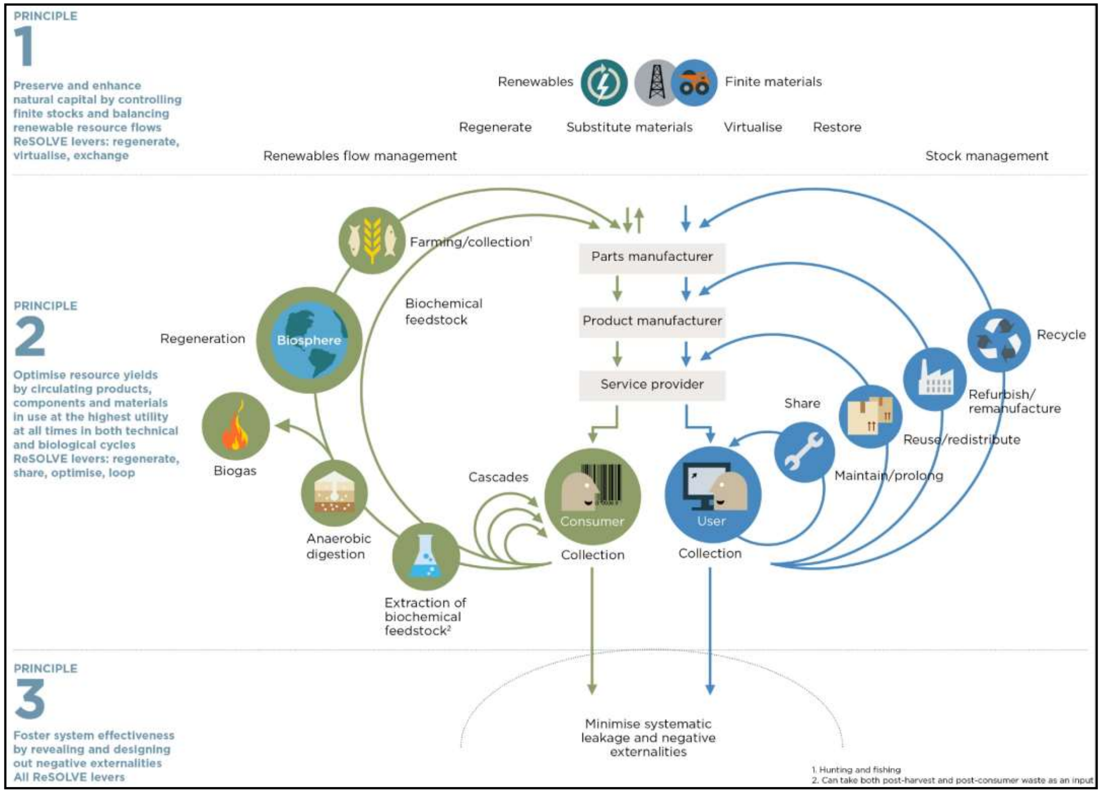
Renewables: the chemical industry

- Seven oil and gas companies have invested $15 bn in renewables over the past four years
- 1,200 climate change laws were adopted
- In 2021, renewable power generation rose by 12%
- Biomass is currently the largest U.S. renewable energy source with more than 200 existing plants



Reference: https://www.ft.com/content/44ed7e90-3960-11e7-ac89-b01cc67cfeec

RENEWABLES AND CIRCULAR ECONOMY



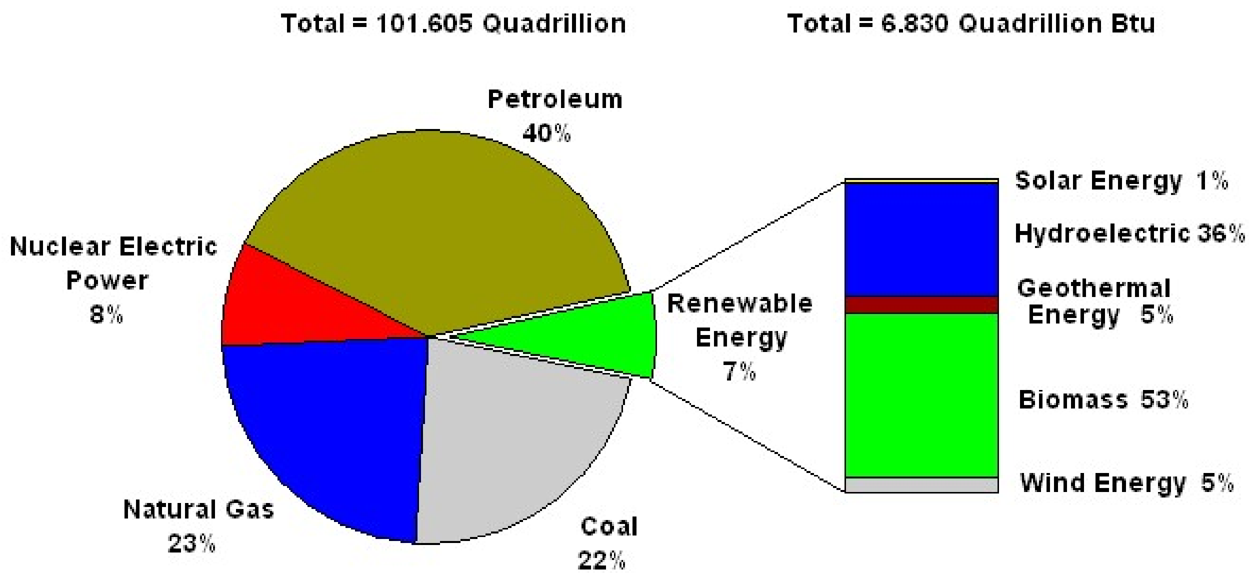
- Circular economy (biological, technical materials)*
  - ~2,5 bin. t/yr of valorizable waste
  - Saving virgin resources - €bn600/yr (< 2030)
  - Economic benefits - €tr1.8/yr (<2030)

2C product registry, Circular Economy Act, FICE, WRAP

**Ellen MacArthur Foundation, 2021*

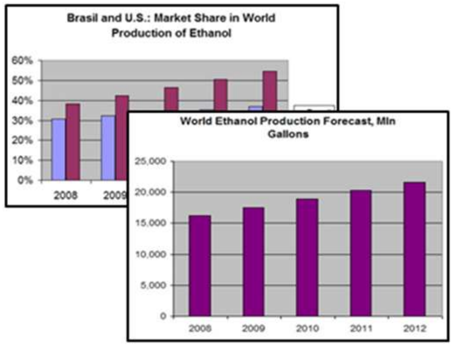
Renewables and the prospects of biomass

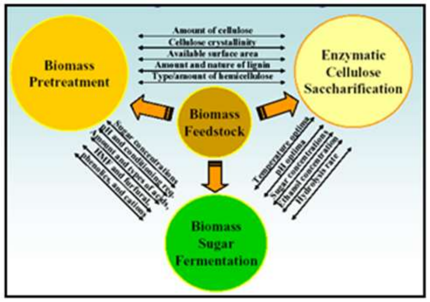
Whereas electric power can be met by other renewable energy technologies….



… biomass is the <u>only renewable source of carbon-based fuels</u>, chemicals and materials

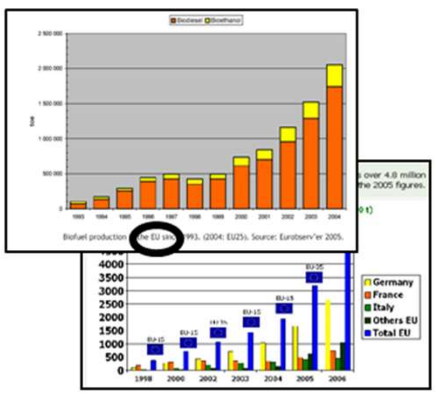
The Experience from First generation developments

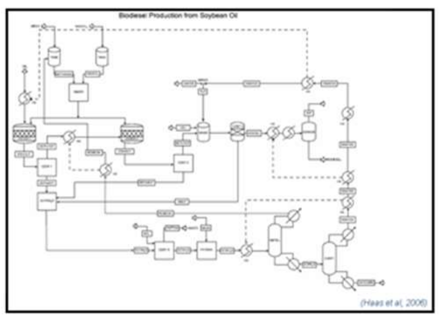




Single, often unsustainable, Resources ⇨ **Parallel**, unconnected processing paths ⇨ **Single** products (mainly biofuel)

First generation developments





- Single feedstocks
- Single products (mainly producing ethanol & biodiesel)
- Limited degree of innovation
- Increasing degree of integration
- Still experimental and developing
- Number of plants continues to increase despite the recent stop set on subsidies

Mature technologies gradually giving their way to entire new developments

Biorefineries and sustainability

First generation plants

- Gate-to-gate: very green
- Cradle-to-grave: not as green

Sustainability

- Large part of the plant remains unused
- Dictates a holistic use of the plant, use of non-food sources
- Consequences of land use (ILUC)
- Logistics, upstream and downstream need be considered

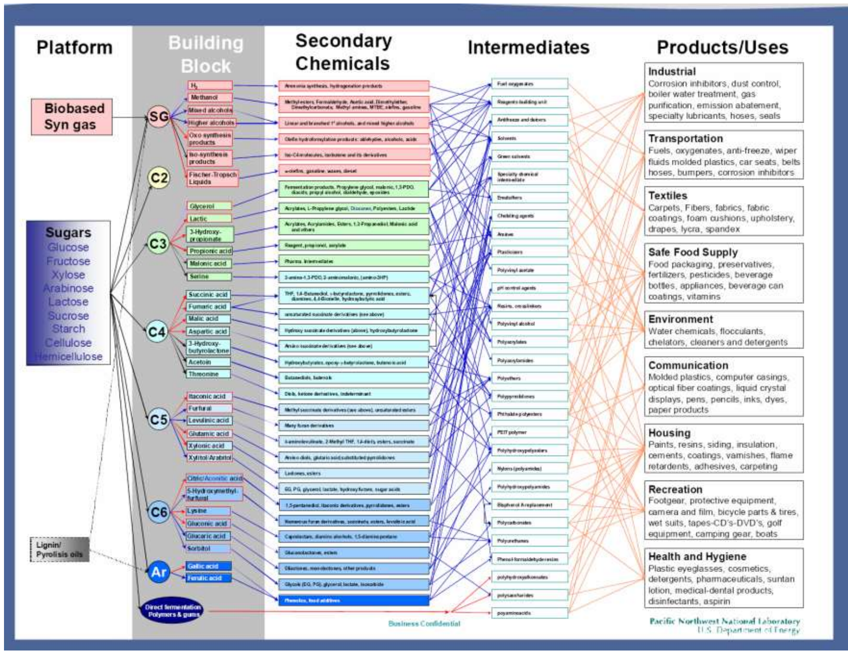
Challenges and opportunities

- Technology to tackle with more difficult feedstocks
- Use feedstocks not used for food
- Large part of available biomass (including waste) remains untapped due to the lack of technology to process it
- Production of multiple products (fuels and chemicals) is both economically and environmentally promising

SECOND GENERATION BIORENEWABLES

All sources of biomass

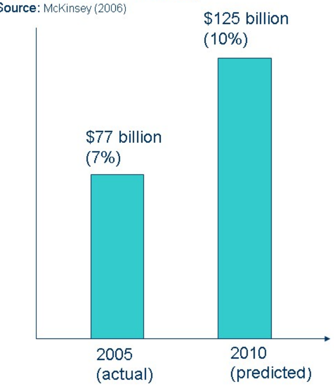
Integration of routes



nates	Generation	Process
Methanol	2°	Thermal
Ethanol	1°& 2°	Biological or Thermal
Butanol	1°& 2°	Biological or Thermal
Mixed alcohols	2°	Thermal
Dimethyl ether	2°	Thermal
Hydrocarbons		
Biodiesel	1°	Physical + chemical
Synthetic diesel	2°	Thermal
Synthetic gasoline	2°	Thermal
Methane	1°& 2°	Thermal
Other		
Hydrogen	1°& 2°	Thermal or Biological

Share of bio-based products in the world chemical industry

Source: McKinsey (2006)



Unknown porfolios

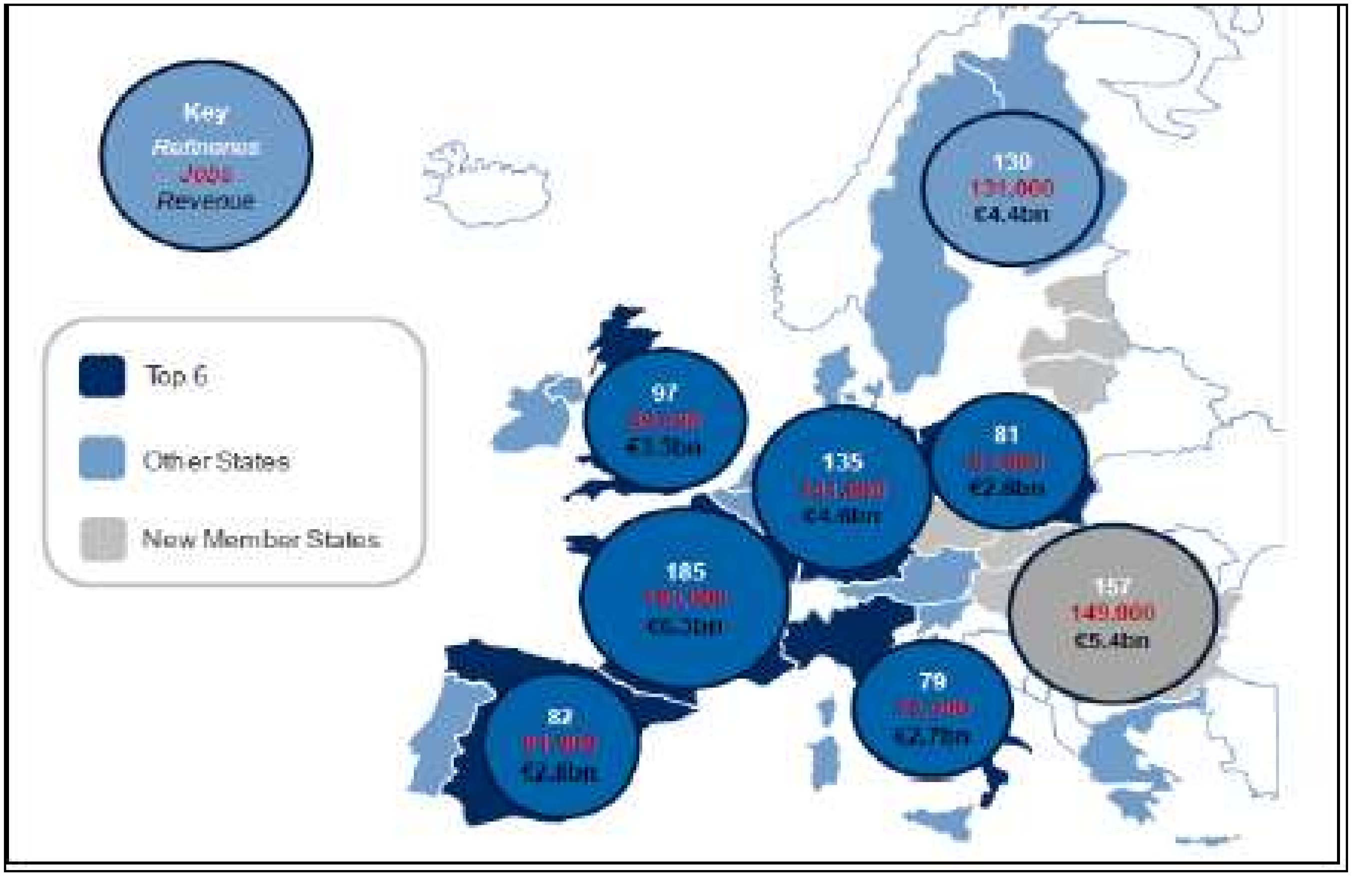
Primary biorefinery

Integration of paths

Second generation developments

- Much bigger problem
- Need for a systematic evaluation and selection of options

THE PICTURE IN EUROPE



Huge socio-economic benefits in the next 10 years

- Over 1,000 new biorefineries
- Revenues in excess of €bn 32
- Over 1 million new jobs

TECHNOLOGY NEEDS

- Scale up successful chemistries to pilots and plants
- Build design expertise to improve material and energy efficiencies
- How? Develop technology to
  - Support scale-up (costing, flowsheeting, screening)
  - Support modular bio refinery concept (regional diversifications)
  - Reduce experimentation with lab chemistries building modeling and flowsheeting capabilities
  - Build process integration technologies
  - Build high-throughput capabilities due to the large number of products and feedstocks

Chemical engineering and PSE perspective

- **Chemical engineering perspective**
  - Similarities to petrochemical industry
    - Exploitation of energy products, not chemicals
    - Gradual evolution, integration and innovation to exploit ‘every drop of oil’ into a useful product
  - Biomass processing: chemical and process engineering problem
    - Multiple products, processes and reaction paths
    - Multiple chemistry and transformation stages, still
      - Multiple feedstocks, regional variability and seasonality
      - Drive towards local rather global solutions with additional incentives to exploit other renewables
- **PSE perspective**
  - **Synthesis** challenges
    - Large combinatorial problem, product against feedstocks and technologies
  - **Process integration** challenges
    - Raw material utilization, energy recovery, environmental performance
  - **Design** and flowsheeting challenges
    - Improve and retrofit flowsheet, innovate with novel process equipment
    - Build the energy **supply chains** of the future
- **ChE and PSE extremely valuable paradigms**

AS SECOND GENERATION BIOREFINERIES ARE GETTING REAL,
LET US TAKE A SMALL TOUR OVER EXISTING DEVELOPMENTS TO GET A FEELING OF THE DESIGN CHALLENGES …

Maabjerg Energy (Denmark)

- State-of-the-art: Commercial
- Type of biorefinery: five-platform (C5&C6 sugars, lignin, biogas, biomethane, electricity and heat)
- Owner: Vestforsying A/S, Struer Forsying, Nomi I/S, Dong Energy A/S, Novozymes A/S
- Feedstocks: Wood chips, straw, manure, sewage sludge, MSW
- Capacity:
  - 300 Kt/y straw; 520 kt manure, 100k t/y MSW, 280kt/y biowaste
  - 80 km3/y bioethanol, 50 Mm3 biogas, 36kt/y lignin, 25,000 households
- Output: bio-methane, bioethanol, fertilizers, electricity and heat

They know that **other products could make better choices** but what to produce?

Alberta pacific forest Ind (Canada)

- State-of-the-art: Commercial scale
- Type of biorefinery: three-platform (pulp, stripper off-gas, electricity and heat)
- Location: Alberta, Canada
- Owner: Alpac Forest Products
- Feedstocks: Wood chips (aspen, poplar, spruce, pine) certified by the Council
- Output:
  - 80 GWh green electricity,
  - 3kt/y methanol,
  - 665kt/y pulp

Additional feedstocks are possible and the product **portfolio should be extended** but how?

INEOS (USA)

- State-of-the-art: Commercial scale
- Type of biorefinery: two-platform (syngas, power & heat) biorefinery using syngas fermentation to produce bioethanol and power
- Location: Feedstocks: Vegetative, yard and MSW
- Output: bioethanol, power

Feedstocks are enough but the product portfolio should be extended. How?

Major Demonstration & pilots

OTHER COMMERCIAL

- CIMV (France); softwood and hardwood; C5&C5, lignin
- Borregard (Norway): forestry wood to Vanillin, Ethanol, polymers
- Crescentino (Italy); giants reeds, miscanthus, switch grass, agricultural residues; C5&C6, lignin

MAJOR DEMONSTRATION

- Inbicon (Denmark); straw, corn stover, bagasse; bioethanol, electricity, heat and power
- Cellulac (Ireland); lignocellulosics for chemicals (LA, PLA); C5&C6, lignin

PILOTS

- Bioliq (Germany); residues; pyrolysis for BtL fuels
- Biogasol (Denmark); straw and agricultural residues; sugar-lignin-biogas

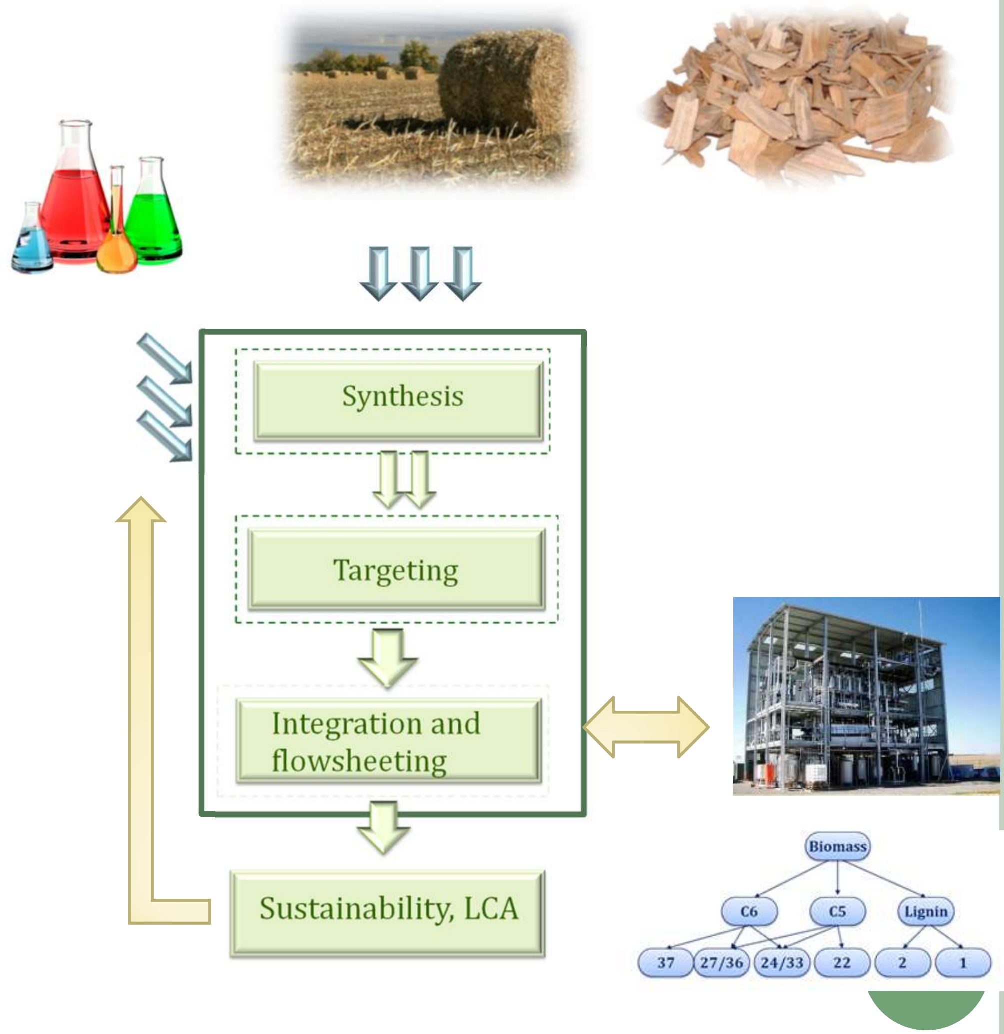
SO,
WHAT IS THE COMMON DESIGN CHALLENGE FOR THE SECOND GENERATION BIOREFINERIES OF TODAY?

TECHNOLOGY READINESS LEVEL

- Powerful teeth with a huge appetite for biomass
- Mid-gut is shaping up
- Hind-gut is still to be developed

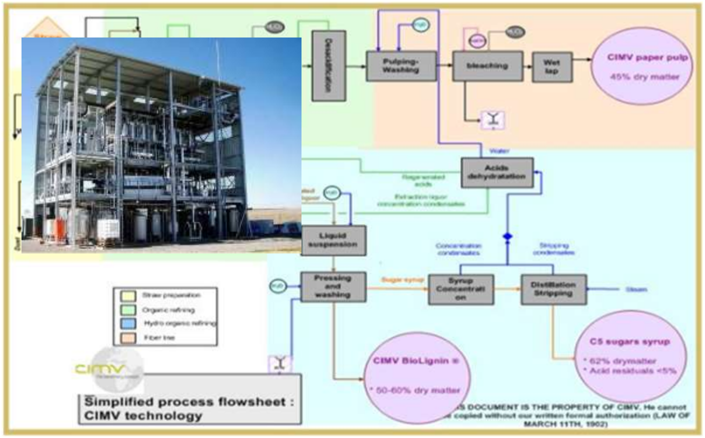
PROBLEM AND AN OUTLINE APPROACH

- Synthesis stage
  - Which products and feedstocks to select
- Targeting stage:
  - scope to integrate and save
- Process development
  - Process flowsheeting and process integration



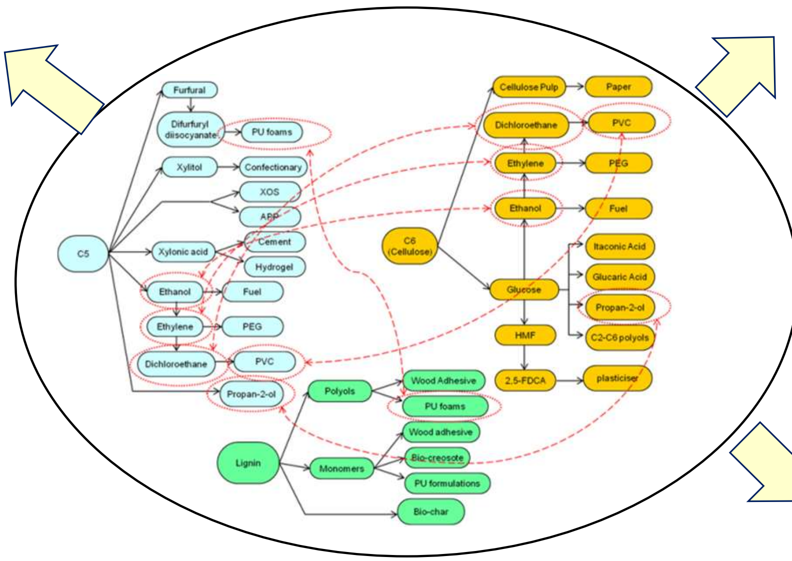
BUILDING 2G PLANTS:
THE CASE OF ORGANOSOLV

DESIGN DECISIONS



- Bulk chemicals: C6, C5, lignin
- Feedstocks: wheat straw, corn stover, rice, bagasse, hardwood
- 85 different products and chemistries

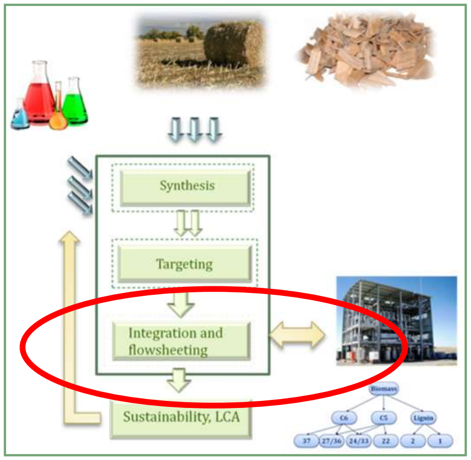
C6 Sugars - Cellulose		
Ranking	**Product Name**	**Price €/tn**
1	Polyamide_1	4000
2	Polyester	7523
3	Polyamide_1	4000
4	HMF_1	5000
5	Propan-2-ol	1667
6	Polyacrylate	1971
7	PEIF	1079
8	Pulp	550
9	Polypropylene1	970
10	Wood_Adhesive 1	500
11	PEF	1079
12	Ethylene_Glycol	800
13	Dichlroethane1	442
14	Bio_PVC1	681
15	2_6_FDCA_Ester	622
16	Glucose	373
17	Sorbitol	583
18	Ethanol1	560
19	Ethylene1	906
20	Isosorbite	502
21	2G_sorbitan_esters	502



C5 Sugars		
Ranking	**Product Name**	**Price €/tn**
1	Xylonic Acid	61370
2	1_2_4_Butanetrio_trinitrate	90000
3	Difurfuryl disocyanate	15000
4	XOS	8500
5	Xylitol	3500
6	APP	2500
7	Hydrogel	1888
8	Bio_Polyester	1483
9	XB_polyester	1750
10	New_Polyamide	1000
11	Dichloroethane2	442
12	Bio_PVC2	681
13	Wood_Adhesive2	360
14	C5_fraction	360
15	Ethanol2	560
16	Ethylene3	906
17	Polypropylene2	970
18	Furfural	597
19	Propylene2	930

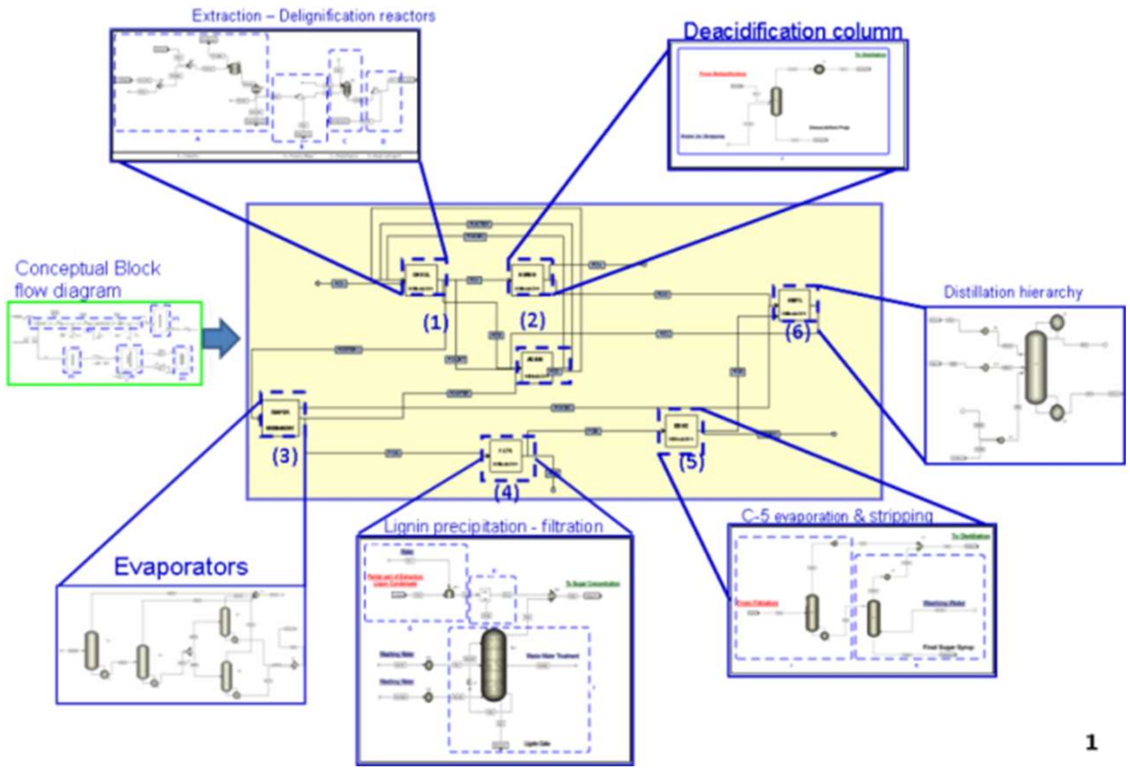
Lignin		
Ranking	**Product Name**	**Price €/tn**
1	Lignin_Castor_Oil	4200
2	BIO_PU_Coating	10000
3	RF_Resin	1076
4	Aromatic_Polyols	1620
5	Vanillin	12000
6	Activated_Carbon	2093
	Phenolic_oligomers	800
	Phenolic_monomers	1750
7	Carbon_Black	835
	Phenolic_oligomers	1076
8	Bio_Char	109
	Pyrolysis Oil	

- Scope for savings: bulk products
- Scope to expand: products and feedstocks
- Scope to integrate production paths of bulk and specialties



BIOREFINERY PLANT:
SAVINGS ON THE PRODUCTION OF BULK CHEMICALS

Scaling up and surrogate models

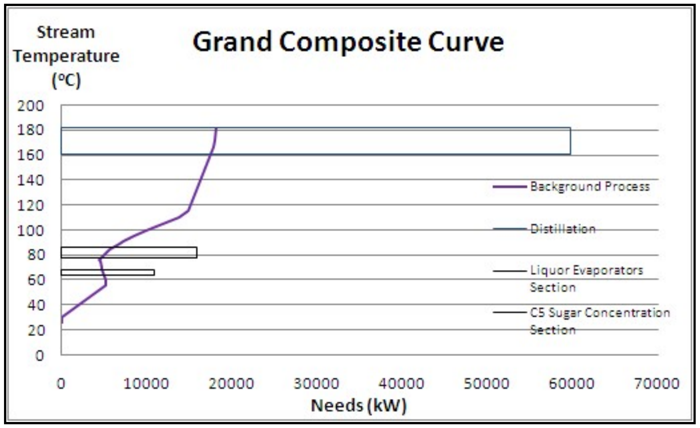


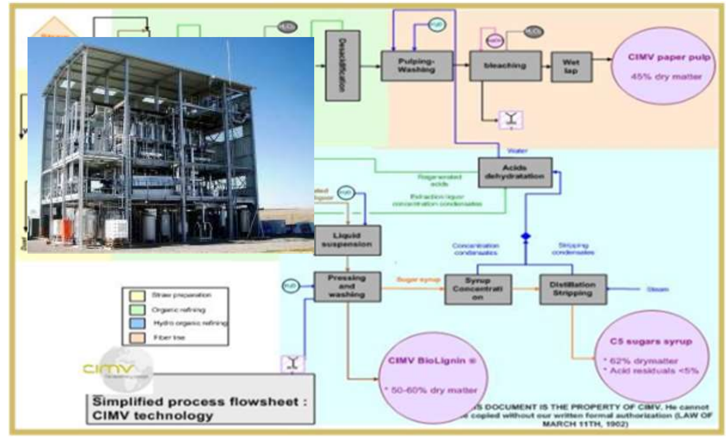
- Modelling: State-of-practice
  - Surrogate models: properties, unit operations
  - Extensive empiricism
  - Intensive communication with plant engineers

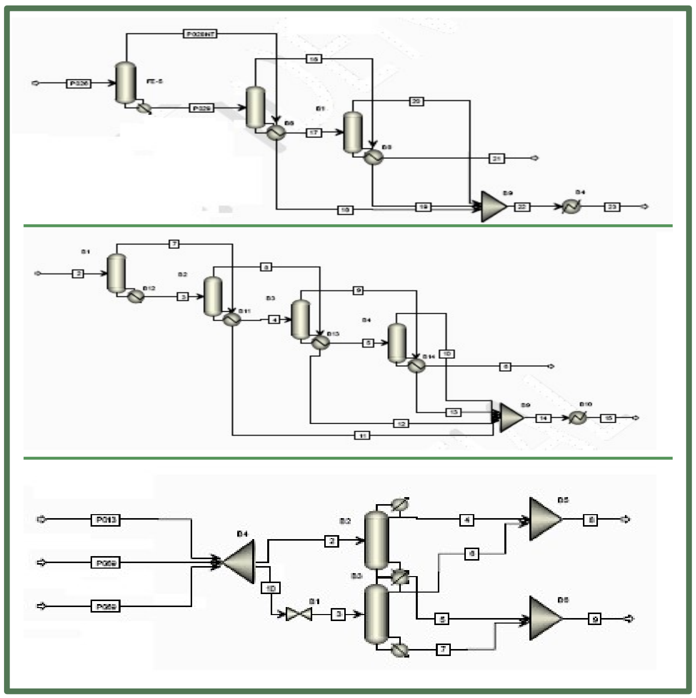
Promising ground of data embedding technologies – design and operations

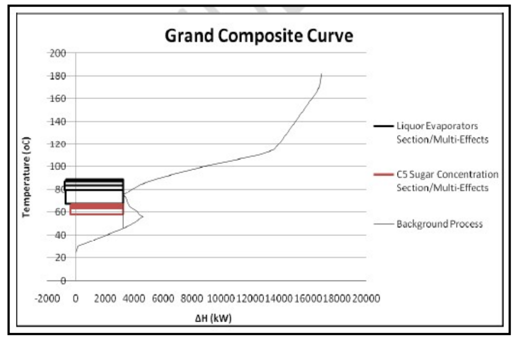
- Hybrid models: combine first-principles with data analytics
- Thermodynamics and stream modelling
  - Representation of non-conventional streams (organic waste, re-used plastics, agricultural residues etc)
  - Multi-scale modelling technology (e.g. integration of modelling scales, GC methods for new substrates etc)
- Thermo-chemical and biochemical processes:
  - Embedding on equation-based models
  - Modelling difficult processes (e.g. HTL, pyrolysis)
  - Development of Digital Twins for bioreactors
- *Essentially most machine learning tools can be deployed for different purposes*

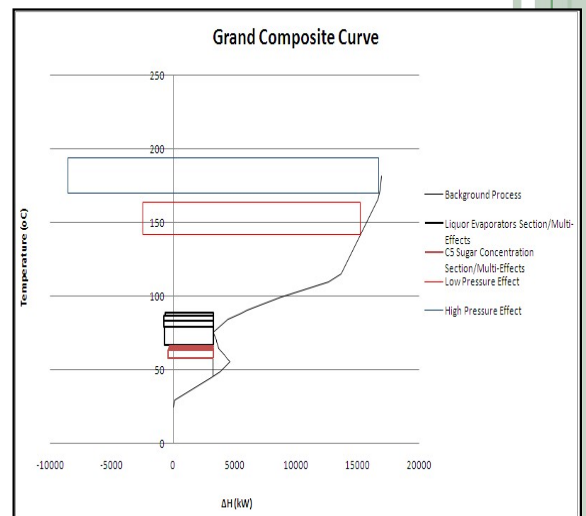
PROCESS MODIFICATIONS AND ENERGY SAVINGS











Before integration:
heating duties = 110.8 MW
cooling duties = 103.4 MW

Integrated process
heating duties = 25.5 MW
cooling duties = 15.7 MW

- Changes already installed (not only targets and expectations)
- Savings mainly through **process modifications** NOT matching **hot and cold streams**

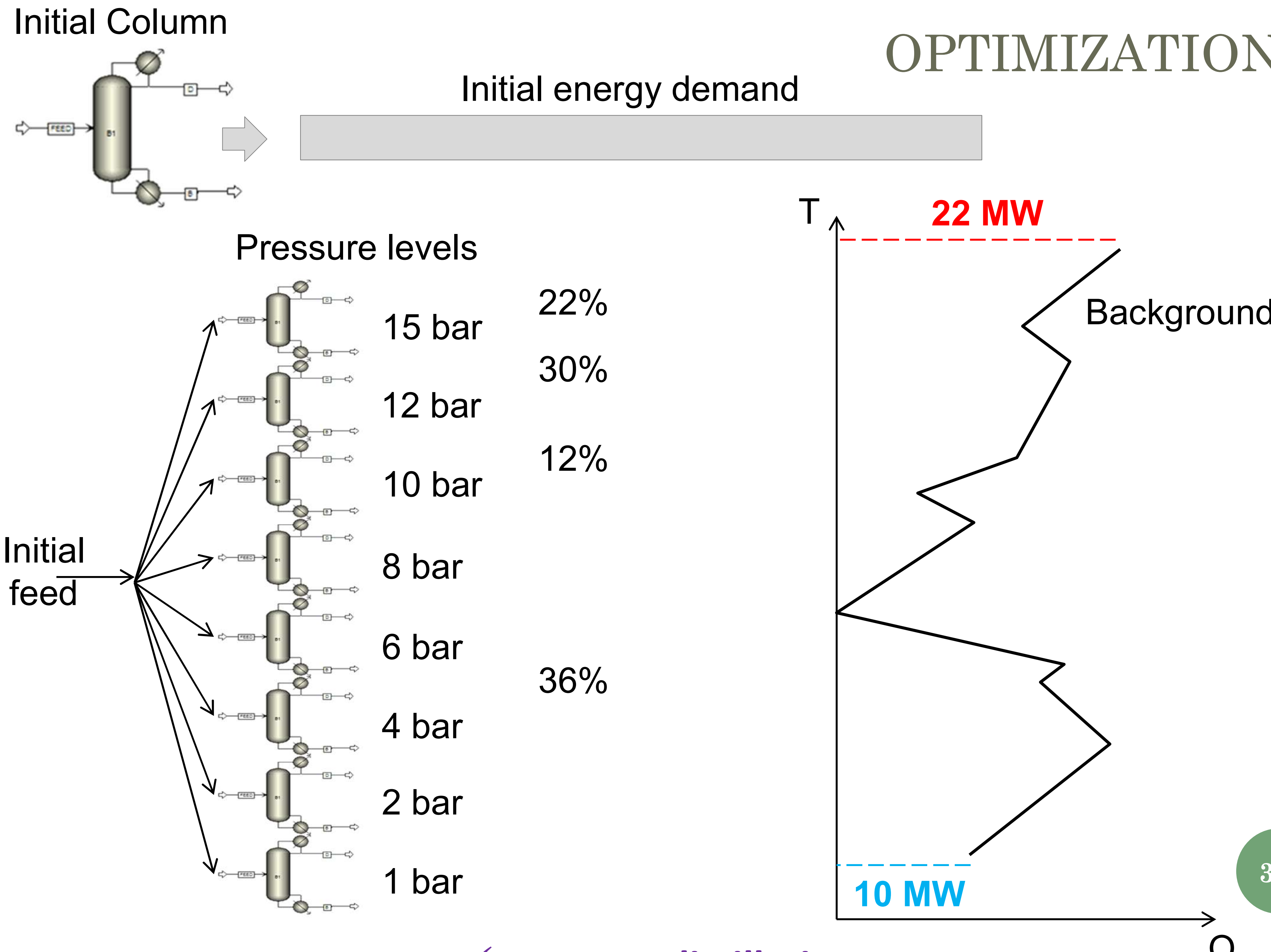
Process integration challenges

- Conventional integration is useful but hot and cold streams are now degrees of freedom
- Conventional methods can be tiresome, essentially impossible to properly apply

THUS

- Unlike conventional applications, both process streams and processes are degrees of freedom
- Manual experimentation does not prepare for high-throughput analysis
- Can we use mathematical optimization to extend thermodynamic models (e.g. without superstructure methods)?

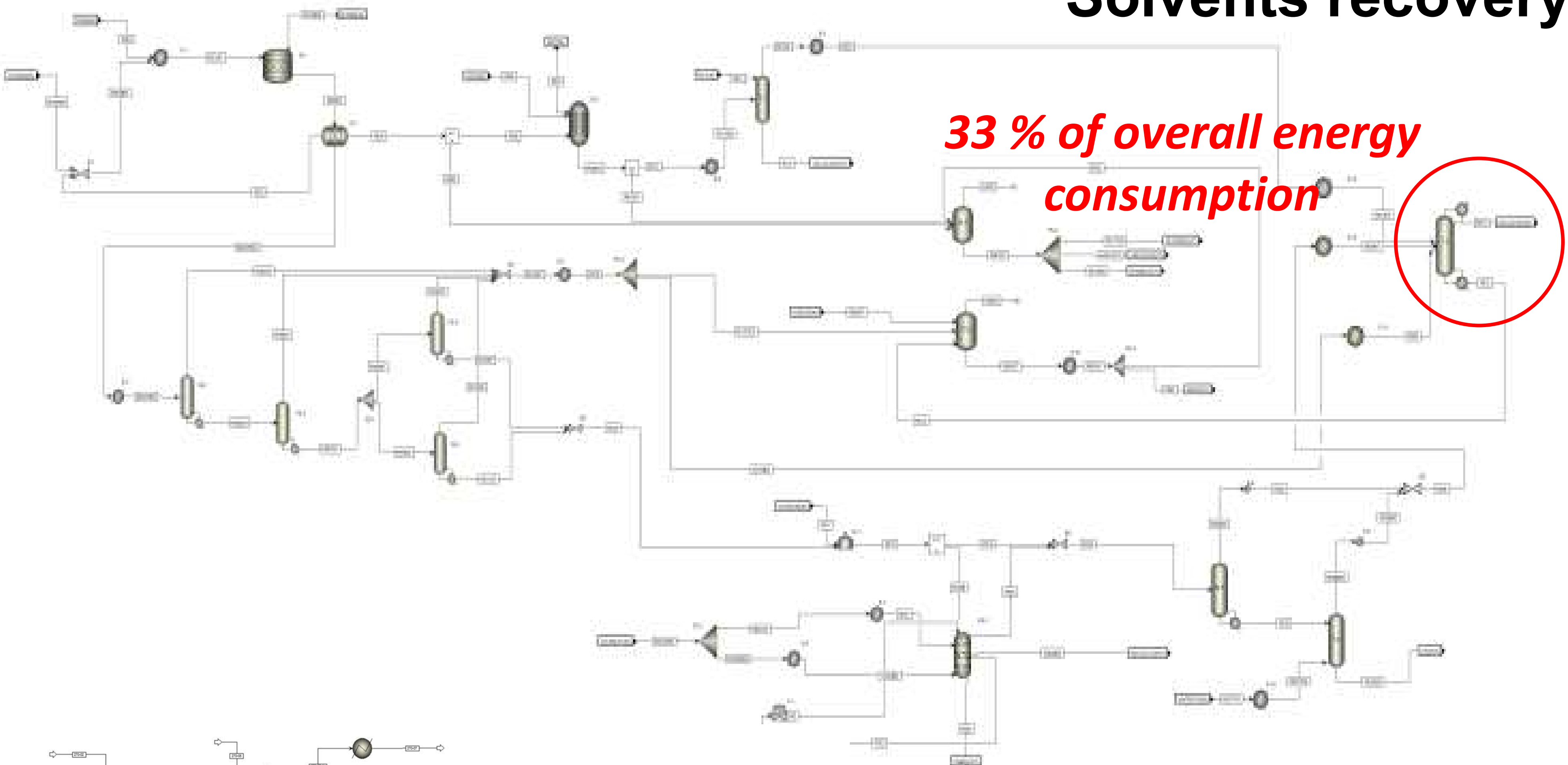
INTEGRATION WITH MATHEMATICAL OPTIMIZATION



✓Zero cost distillation

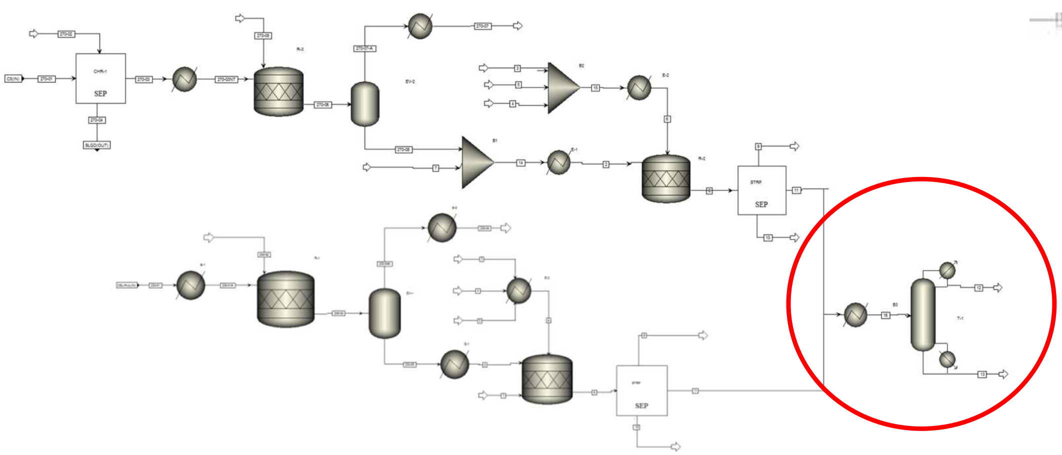
Integration with mathematical optimization

Solvents recovery



33 % of overall energy consumption

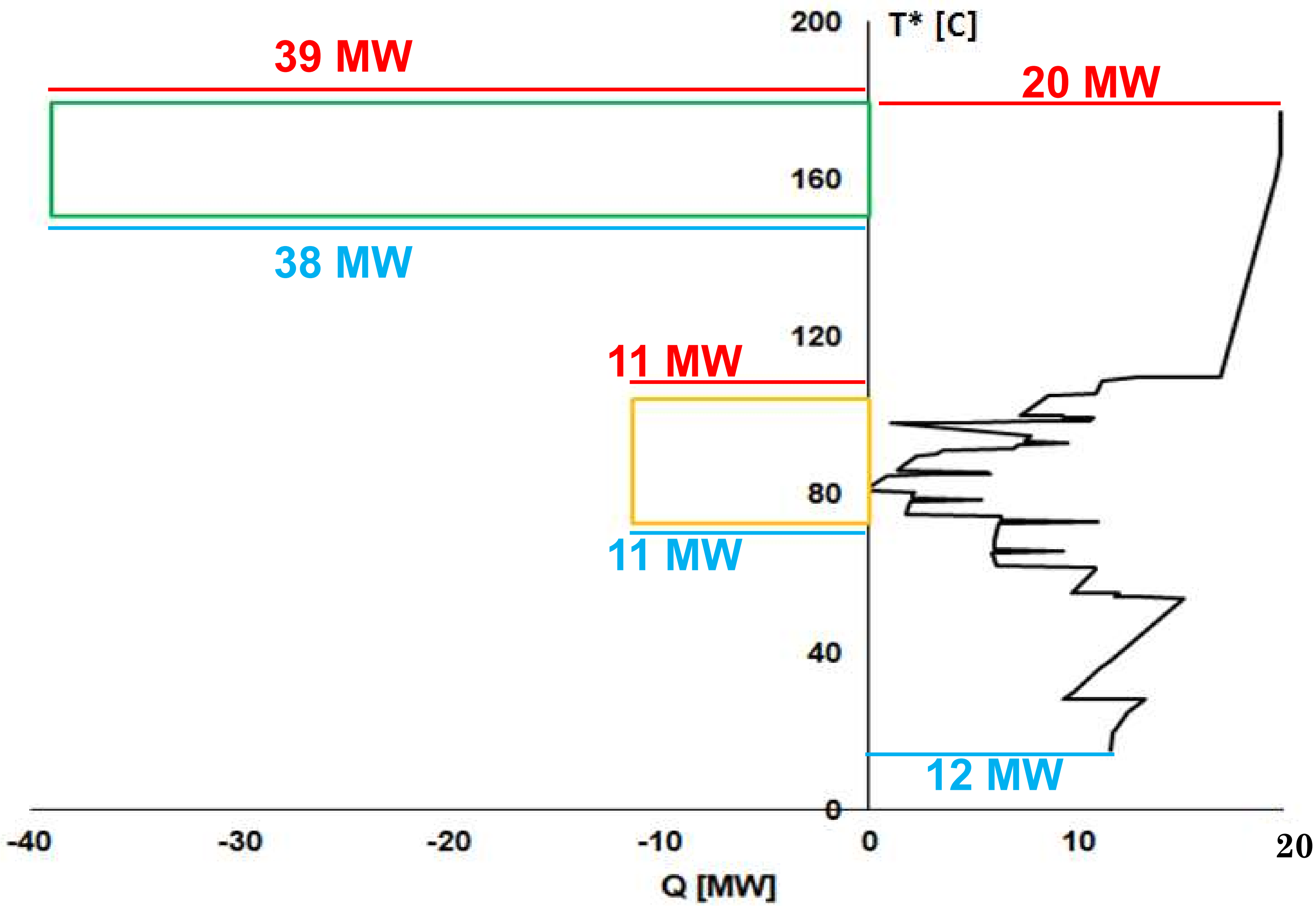
Ethanol production



10 % of overall energy consumption

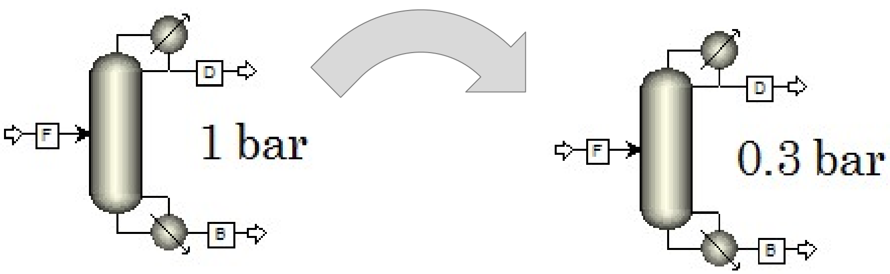
Non-integrated Separations

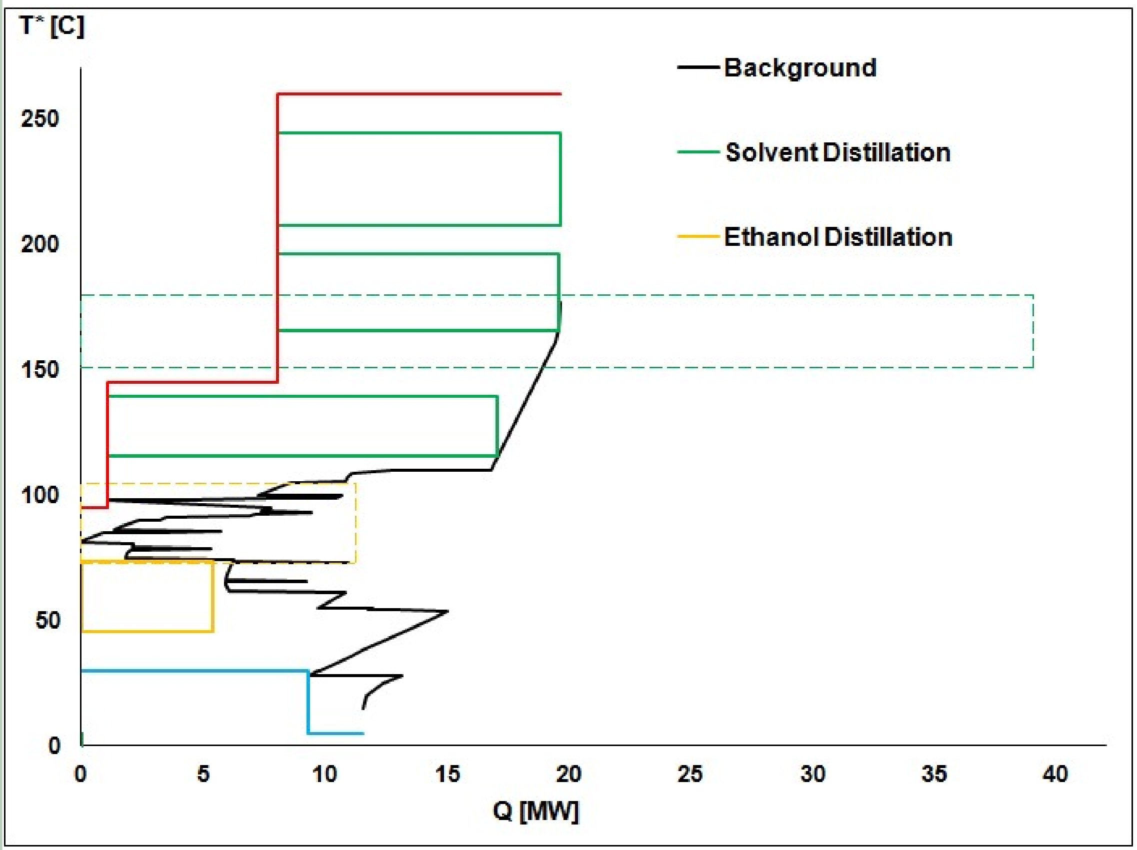
Grand Composite Curve



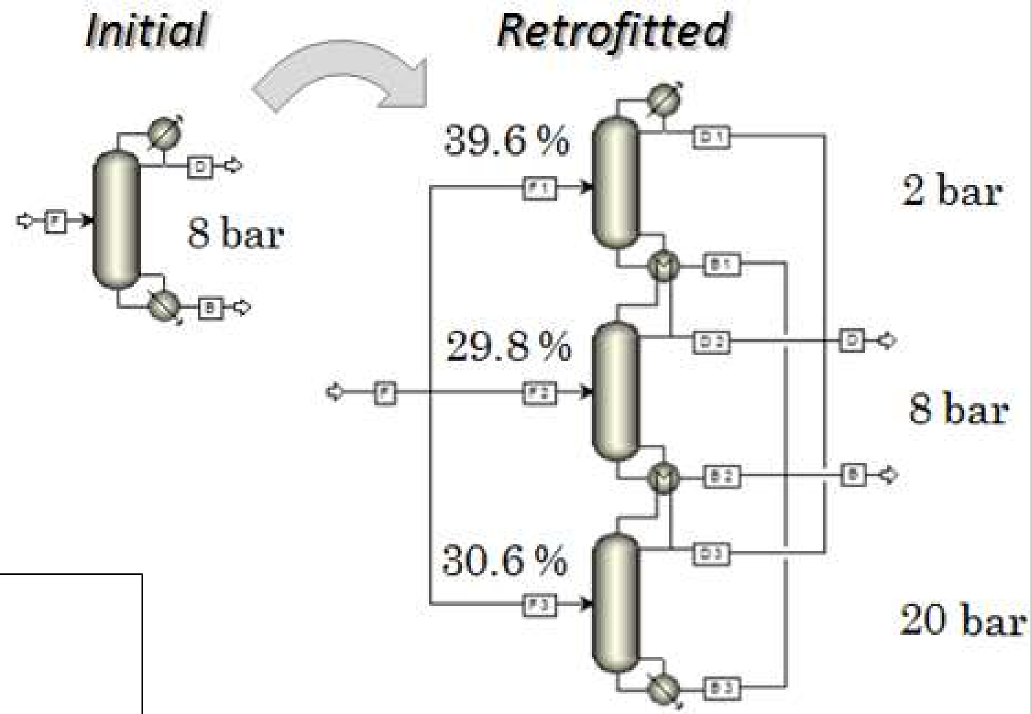
Optimal Distillation Design

pressure re-engineering





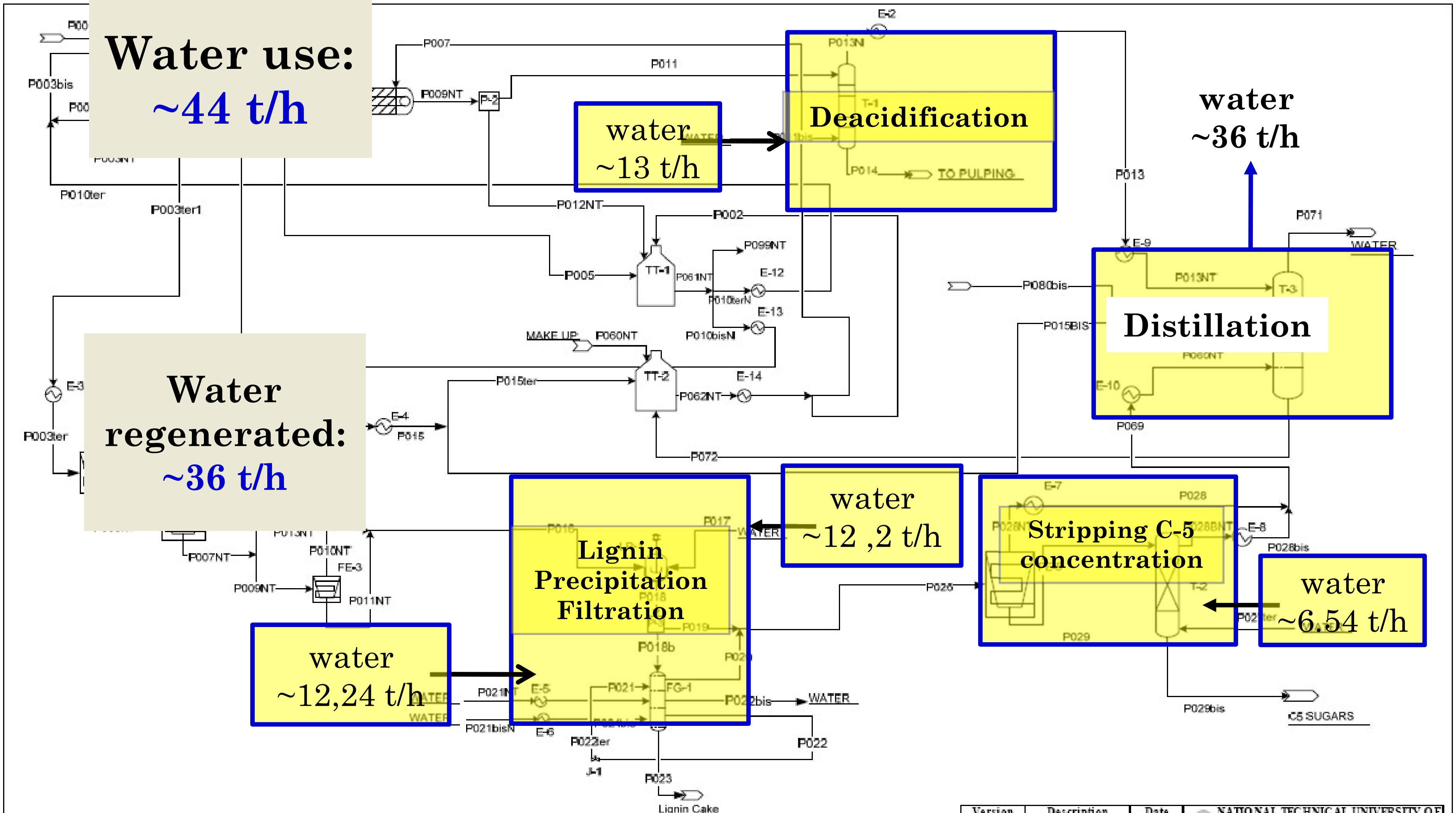
3-effect system



	Base case	Solution	Savings
Steam [MW]	70	19	72 %
Cooling [MW]	61	11	81 %
Energy cost	4.6	1.5	67 %
CAPEX [ME]	2.9	5.3	-

(+83 %)

WATER USE: A MAJOR DRIVE



Deacidification: removes 6.35 t/h of AA and 3.87 t/h of FA

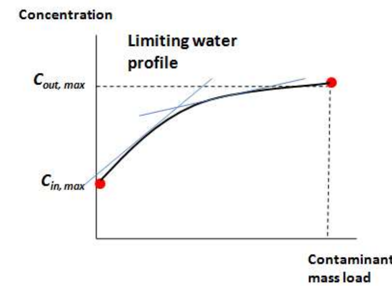
Lignin precipitation – filtration: removes 4 t/h of AA and 3.3 t/h of FA

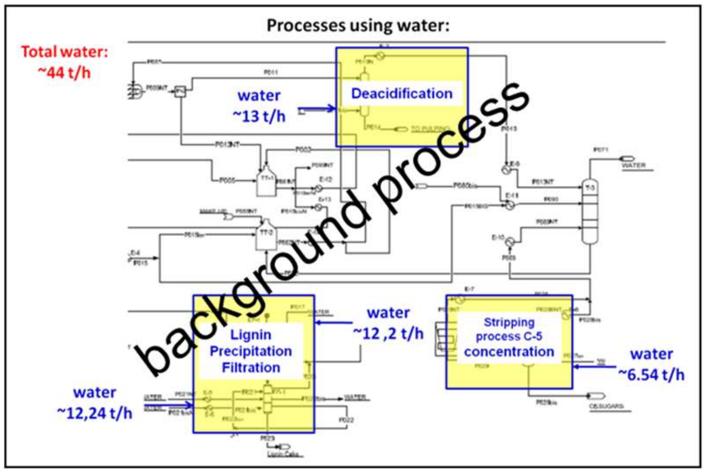
C-5 Sugars– stripping process : removes 1.2 t/h of AA and 0.03 t/h of FA

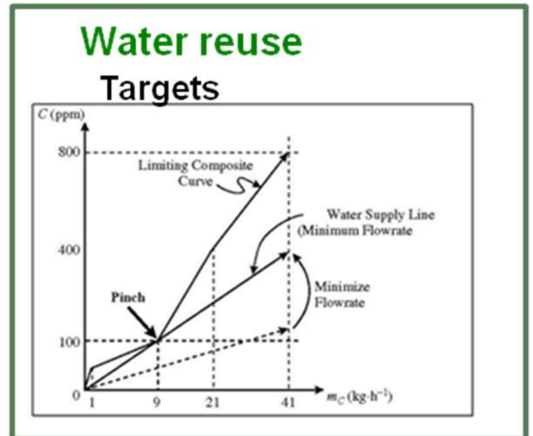
Water integration: conventional methods fail

- Large deviations from usual assumptions: non-ideal mixtures
- Water profile collapse as
  - $m^w = m^w(C^{in,max}, C^{out,max})$
  - $C_i^{out} = C_i^{out}\left(C_1^{in},\dots,C_i^{in},\dots,C_m^{in}\right)$
  - Non dilute mixture – non linear water profiles

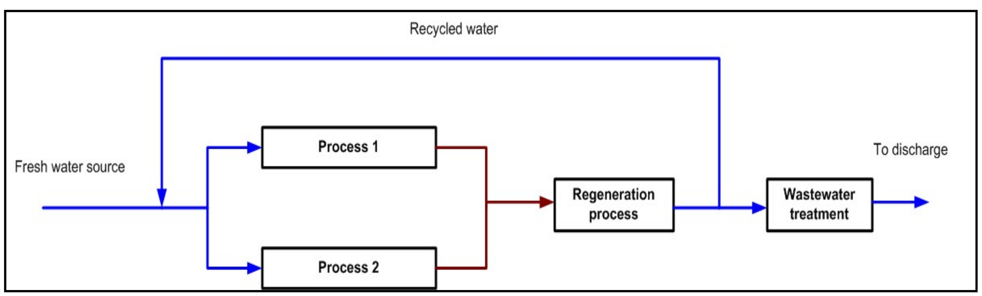
$$\frac{m_i}{m_i + m_w} \neq \frac{m_i}{m_w}$$

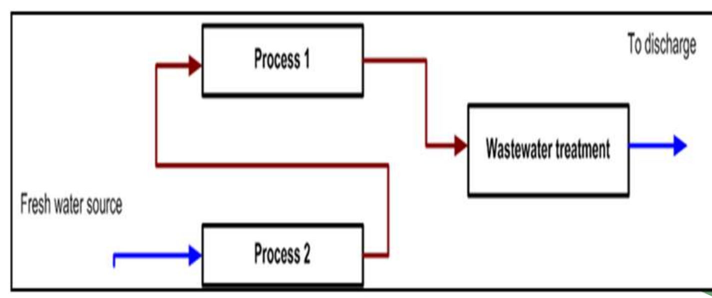






Superstructure optimization





- Decomposition better, still not enough

A PROBLEM DECOMPOSITION APPROACH

- sets

water-using processes

$I = \{i \mid i = 1, 2, \dots, N_I\}$

components

$C = \{c \mid c = 1, 2, \dots, Nc\}$

freshwater sources

$J = \{j \mid j = 1, 2, \dots, N_J\}$

concentration intervals

$CI = \{k \mid k = 1, 2, \dots, K\}$

MILP:

$$\min S = \sum_{j \in J} c_j Fw_j$$

s.t.:

$$s_{c,i,k} - s_{c,i,k-1} + \sum_j M_{c,i,j,k} \ge M^P_{c,i,k}, \quad k \in CI,\ i \in I,\ c \in C$$

$$\sum_i M_{c,i,j,k} \le M^W_{c,j,k}$$

$$M^W_{c,j,k} = Fw_j (C_{c,k} - C_{c,k+1})$$

$$0 \le Fw_j \le Fw_j^U$$

$$Fw_j \ge H_i(C_{c,k}) - FU \cdot (1 - y_{i,j,k}), \quad i \in I, j \in J \text{ and } c \in C$$

$$y_{i,j,k} \ge \frac{M_{c,i,j,k}}{MU_{c,i}}, \quad c \in C$$

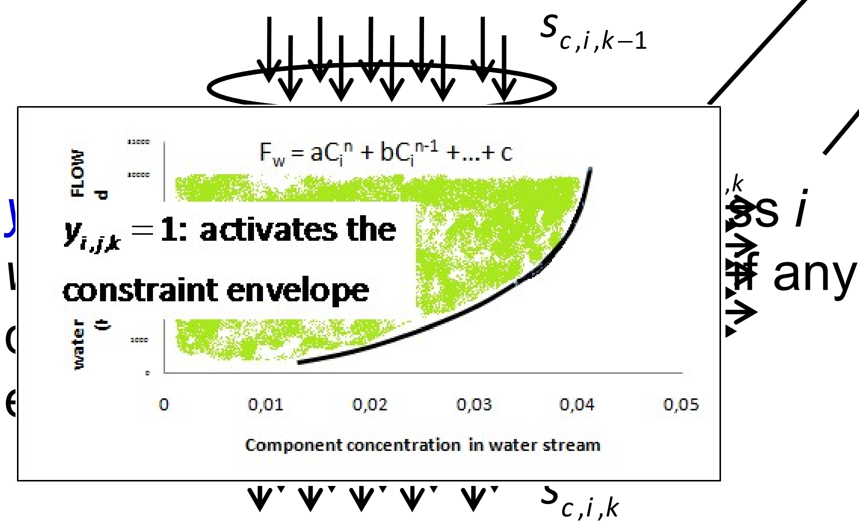
$$M^{TOT}_{c,i,j} = \sum_k M_{c,i,j,k}$$

$$M^{TOT}_{c,i,j} - MU_{c,i} y_{c,i,j} \le 0$$

$$y_{c,i,j} = y_{c',i,j} \quad c \ne c' \in C,$$

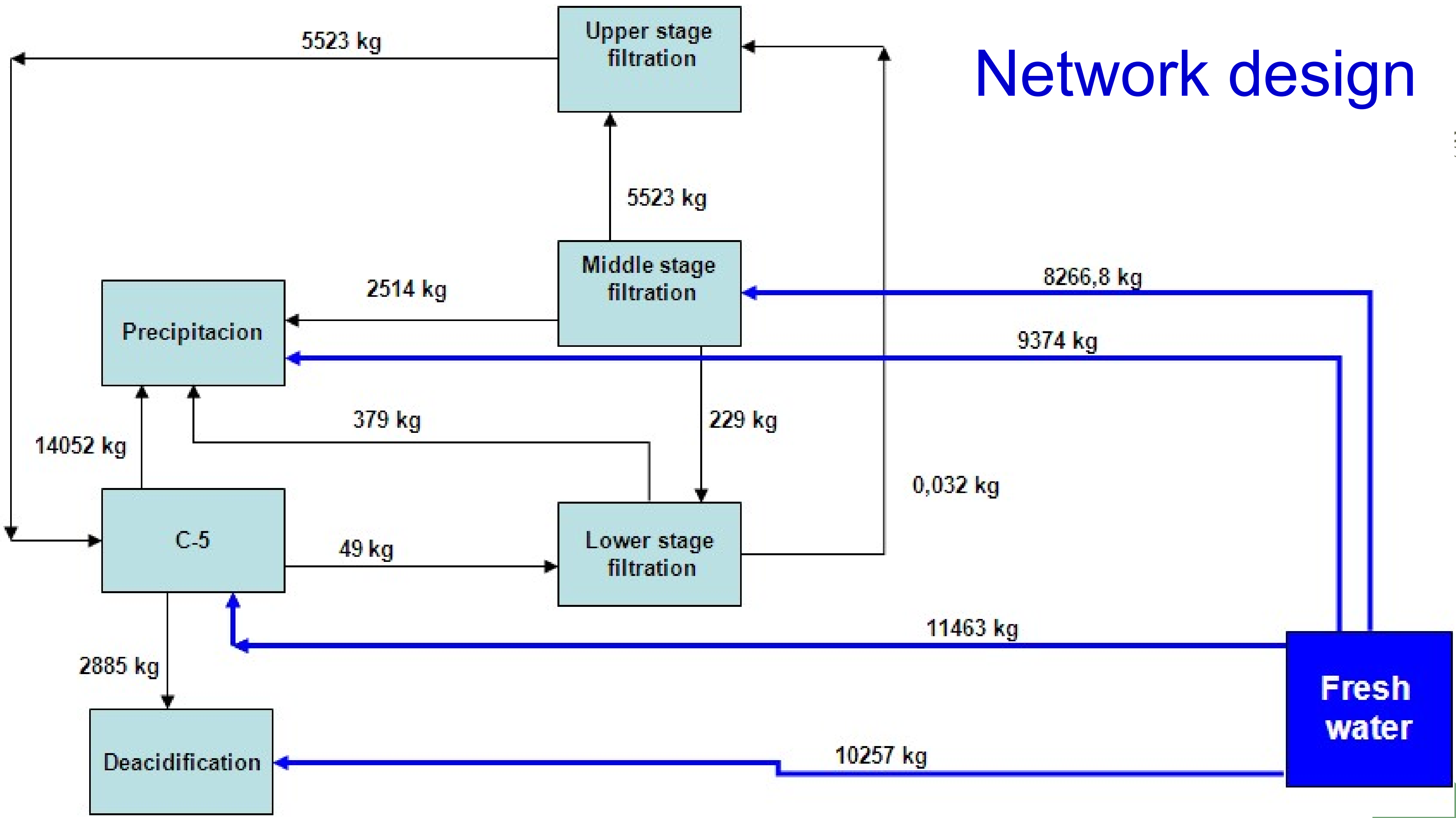
$$s_{c,i,o} = s_{c,i,K} = 0, \quad s_{c,i,k} \ge 0, \quad k = 1, 2, \dots K-1$$

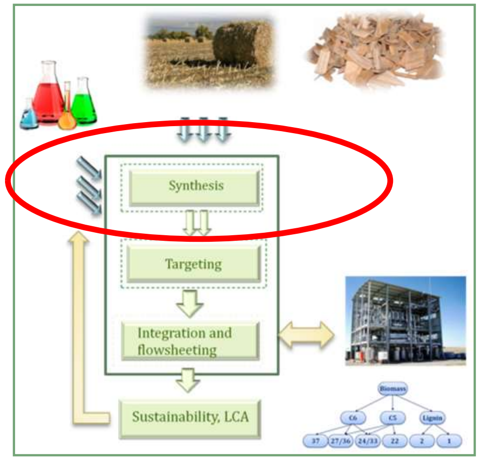
$$y_{c,i,j}, y_{i,j,k} \in \{0,1\}$$



Superstructure Optimization – maximum re-use

Fresh water flow of 29.36 t/h satisfies needs





BIOREFINERY PLANT: SELECTING PRODUCTS, PATHS AND FEEDSTOCKS

BBR and Petri nets as building blocks to the biorefinery superstructure

Building Elements

Raw Materials
- Wood Residues
- Plant Oil
- Animal Fats

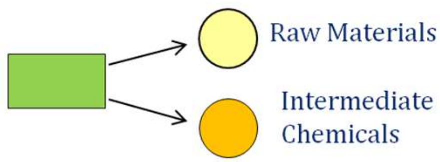
Intermediate Chemicals
- Syngas
- Methanol
- Biogas

Process
- Indirect Gasification
- Direct Gasification
- Synthesis

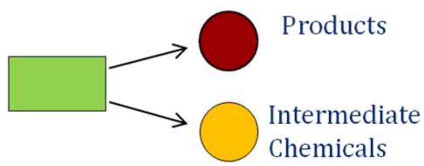
Products
- Ethylene
- Propylene
- PVC

Connectivities

a) A process connects

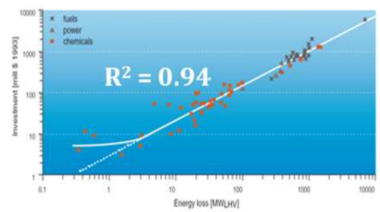


b) A process connects



Cost & Models

- Regression models based on thermodynamics

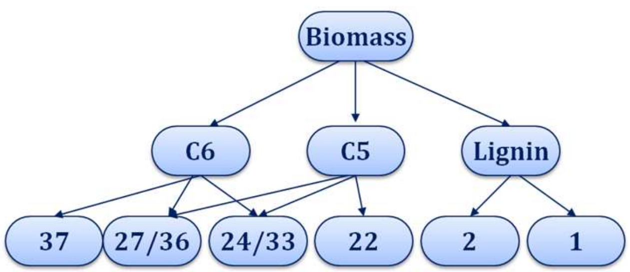


Investment [\$M 1993] = 3.0*(Energy losses [MW])$^{0.84}$

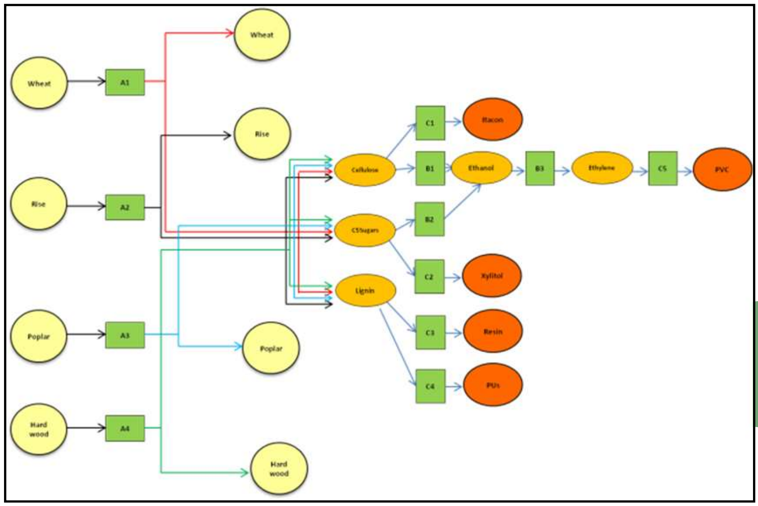
Energy losses = $LHV_{(feed + fuel)}$ - $LHV_{(product)}$

$LHV_{(feed + fuel)}$, $LHV_{(product)}$ – lower heating values of feed and fuel of process and products (multiplied by the hourly flows of materials)

- Objective function
  - Cost/Profit
  - GHG emissions
- Parameters
  - Cost parameters (prices, market demands)
  - Process parameters (conversions, energy efficiencies)
- Constraints
  - Mass and energy balances
  - Balances at splitters, mixers
  - Market constraints
  - Cost equations
  - Logical constraints
- Variables
  - Continuous variables
    - Process variables (flowrates, split fractions)
    - Economic (cost functions, income streams
  - Binary variables
    - Selection of a process in the solution (1- selected, 0 - rejected)
- Mixed-integer Linear Programming problem



Pilots:
PUs(1), Resins(2), Xylitol (22), EtOH (24/33), PVC (27/36), Itaconate(37)

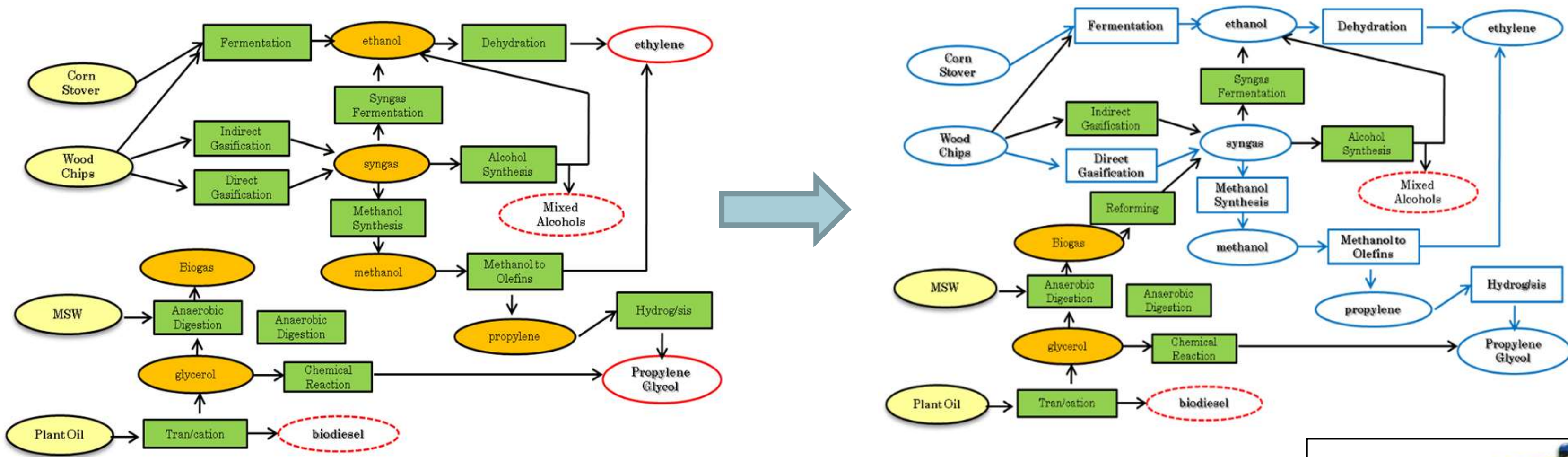


Propylene glycol: Selection of feedstocks and paths

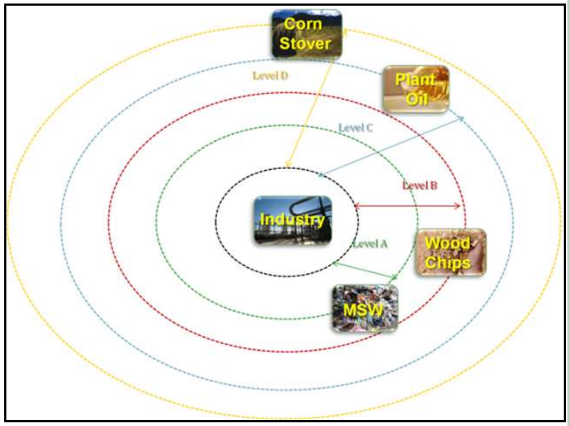
Biomass Types Available:
- Corn Stover
- Wood Chips
- MSW
- Plant Oil

Constrains
- Ethylene Productivity: 50000 t/yr
- Propylene Glycol: 5000 t/yr
- Biomass Availability 250 (of each type) t/yr

Technologies:
- Fermentation
- Direct Gasification
- ...



- Analysis over economic parameters
- Pareto fronts againts primal objectives (GHG, land use)
- Different layouts of supply points



ACETONE: SELECTION OF CO-PRODUCTS

Problem Description

Input Data

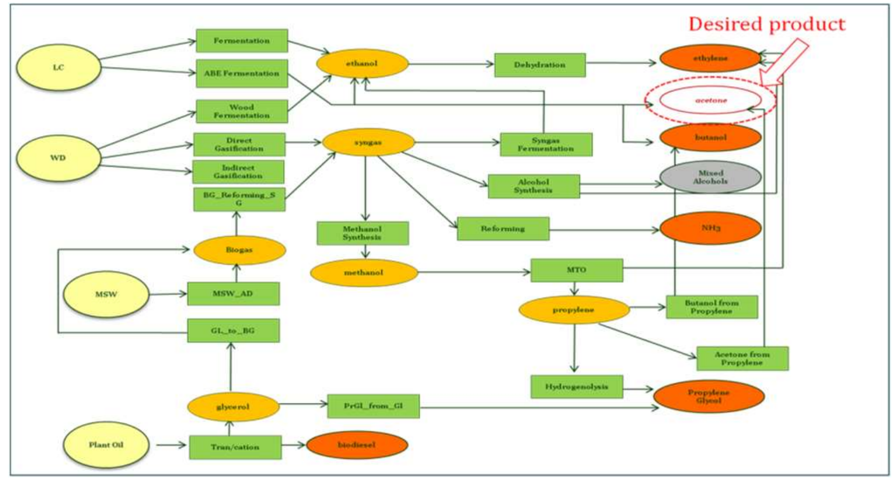
- **Types of Biomass:**
  - Corn Stover
  - Wood Chips
  - MSW
- **Technologies:**
  - Fermentation
  - ABE Fermentation
  - ...

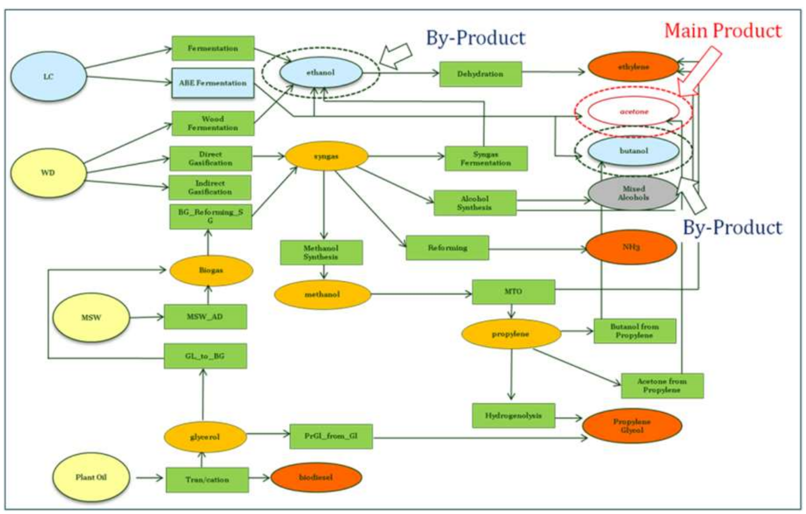
Output Data

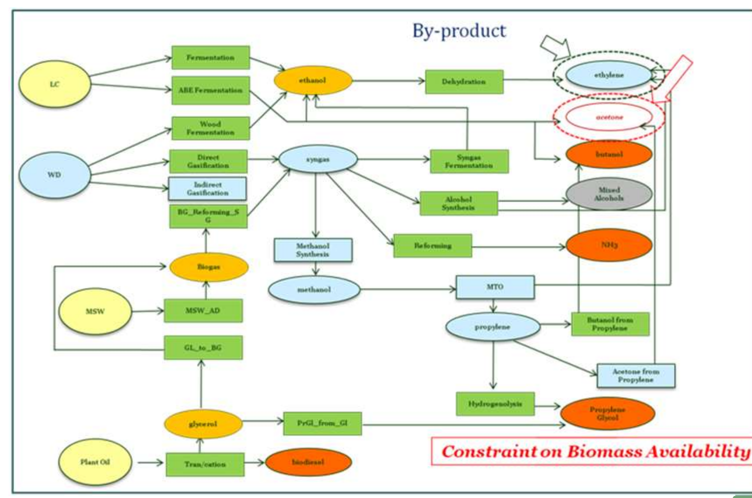
- **Type of biomass or combination**
- **Selected Technologies**
- **By-Products**

Market Demand

- Acetone Production 30 kt/yr



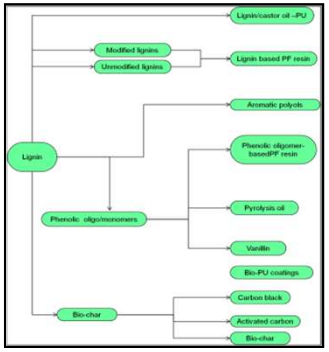


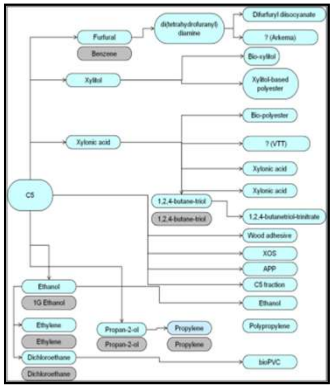


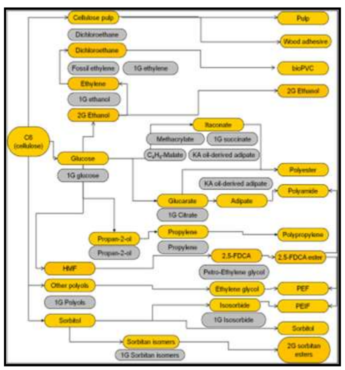
- Unlimited feedstock
- Co-products: Ethanol, butanol

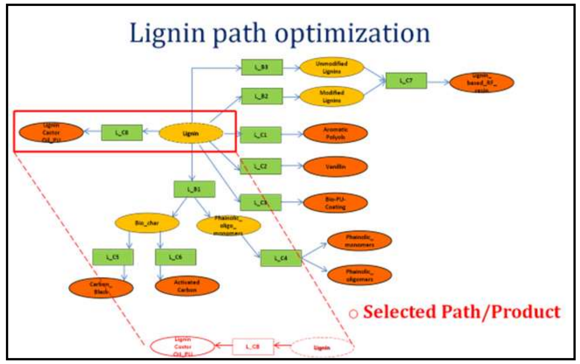
- Constraint feedstock
- Co-products: Ethylene

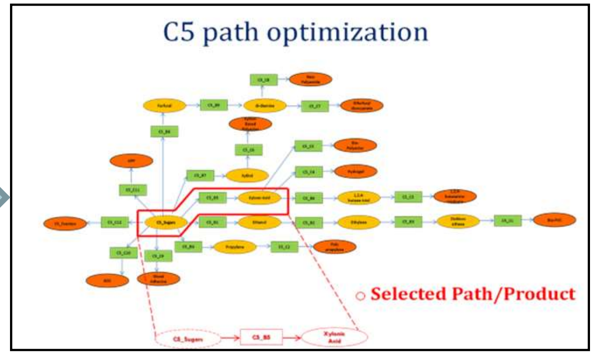
Scoping for unknown of product portfolios

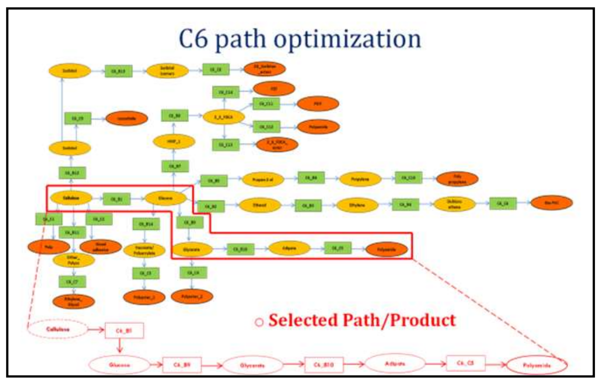












Lignin		
Ranking	Product Name	Price €/tn
1	Lignin_Castor_Oil	4200
2	BIO_PU_Coating	10000
3	RF_Resin	1076
4	Aromatic_Polyols	1620
5	Vanillin	12000
6	Activated_Carbon	2093
	Phenolic_oligomers	800
	Phenolic_monomers	1750
7	Carbon_Black	835
	Phenolic_oligomers	1076
8	Bio_Char	109
	Pyrolysis Oil	

C5 Sugars		
Ranking	Product Name	Price €/tn
1	Xylonic Acid	61370
2	1_2_4_Butanetrio_trinitrate	90000
3	Difurfuryl disocyanate	15000
4	XOS	8500
5	Xylitol	3500
6	APP	2500
7	Hydrogel	1888
8	Bio_Polyester	1483
9	XB_polyester	1750
10	New_Polyamide	1000
11	Dichloroethane2	442
12	Bio_PVC2	681
13	Wood_Adhesive2	360
14	C5_fraction	360
15	Ethanol2	560
16	Ethylene3	906
17	Polypropylene2	970
18	Furfural	597
19	Propylene2	930

C6 Sugars - Cellulose		
Ranking	Product Name	Price €/tn
1	Polyamide_1	4000
2	Polyester	7523
3	Polyamide_1	4000
4	HMF_1	5000
5	Propan-2-ol	1667
6	Polyacrylate	1971
7	PEIF	1079
8	Pulp	550
9	Polypropylene1	970
10	Wood_Adhesive 1	500
11	PEF	1079
12	Ethylene_Glycol	800
13	Dichlroethane1	442
14	Bio_PVC1	681
15	2_6_FDCA_Ester	622
16	Glucose	373
17	Sorbitol	583
18	Ethanol1	560
19	Ethylene1	906
20	Isosorbite	502
21	2G_sorbitan_esters	502

- Selection and ranking is a possible function
- How about LCA? Impossible to apply at early stages unless…

FURTHER PRUNING: LCA

Cellulose

Product name	Economic: Rank (Econ)	Economic: Plant profit	Economic: Profit [%]	Economic: Price € / t	Economic: CAPACITY t / y	Greenhouse gases: Rank (GHG)	Greenhouse gases: GHG balance t CO_2 eq. / t	Greenhouse gases: Reference product t CO_2 eq. / t
Polyamide_1	1	2,76E+07	110	4000	32400	1	-4,8	-6,4
Polyester_1	2	2,66E+07	106	7523	23760	12	-0,4	-2,7
Polyamide_2	3	2,64E+07	105	4000	39420	5	-2,3	-6,4
HMF_2	4	2,63E+07	105	5000	30000			
Propan_2_ol_1	5	2,57E+07	102	1667	55800	7	-0,7	-1,9
Polyacrylate	6	2,55E+07	101	1971	34200	2	-3,4	-6,8
PEIF	7	2,53E+07	100	1079	41310	14	-0,2	-1,8
PEF	8	2,52E+07	100	1079	33480	8	-0,6	-2,7
Pulp	9	2,52E+07	**100**	550	75000	19	0,4	-0,4
Polypropylene_1	10	2,52E+07	100	970	39060			
Wood_adhesive2	11	2,52E+07	100	500	75000	3	-3,4	-4,2
bioPVC1	12	2,51E+07	100	681	68428	21	0,5	-2,0
Glucose_2	13	2,51E+07	100	373	60000	16	0,2	-0,5
Ethylene_glycol	14	2,51E+07	100	800	39000	15	-0,1	-1,6
Ethylene_4	15	2,50E+07	99	906	19440	18	0,3	-1,4
2G_Ethanol_2	16	2,50E+07	99	560	32400	10	-0,5	-2,2
Dichloroethane_4	17	2,50E+07	99	443	68429			
2_5_FDCA_ester	18	2,49E+07	99	622	37800	9	-0,5	-2,6
Isosorbide	19	2,49E+07	99	502	33314			
Sorbitol_2	20	2,49E+07	99	583	32250	20	0,4	-0,5
2G_sorbitan_esters	21	2,48E+07	99	502	33282			
Itaconic acid for polyamide						4	-3,2	-6,4
Itaconic acid for SB rubber						6	-1,0	-2,9
Polyester_1						11	-0,4	-1,8
Polyester_1						13	-0,3	-1,8
Glucarate_2						17	0,2	-0,5

C5 Sugars

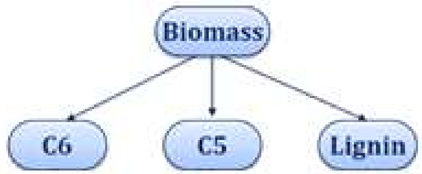
Product name	Economic: Rank (Econ)	Economic: Plant profit	Economic: Profit [%]	Economic: Price € / t	Economic: CAPACITY t / y	Greenhouse gases: Rank (GHG)	Greenhouse gases: GHG balance t CO_2 eq. / t	Greenhouse gases: Reference product t CO_2 eq. / t
Xylonic_acid_2	1	2,76E+07	350	61370	70470	9	0,2	-0,5
1_2_4_butanetriol_trinitrate	2	2,08E+07	264	90000	14515	1	-2,9	-8,4
Difurfuryl_diisocyanate	3	1,09E+07	138	15000	21384	3	-1,7	-4,1
XOS	4	9,72E+06	123	8500	23040	12	0,6	-0,1
Bio_xylitol	5	8,59E+06	109	3500	25200		?	?
APP	6	8,43E+06	107	2500	27720	6	-0,1	-2,3
Name_VTT (Hydrogel)	7	8,37E+06	106	1888	32400			
Bio_polyester	8	8,24E+06	104	1483	32400			
Xylitol_based_polyester	9	8,20E+06	104	1750	25200			
New_polyamide	10	7,90E+06	100	1000	18475	2	-2,1	-6,0
C5_fraction	11	7,89E+06	**100**	360	36000		(?)	-1,1
Polypropylene	12	7,85E+06	99	970	10080	8	0,1	-2,0
Ethanol_2	13	7,85E+06	99	560	18000	5	-0,3	-2,2
Ethylene_2	14	7,84E+06	99	906	10800	10	0,3	-1,4
Propylene_2	15	7,84E+06	99	930	10080			
bioPVC	16	7,83E+06	99	681	22429	11	0,4	-2,0
Dichloroethane_2	17	7,82E+06	99	433	38016			
Furfural_2	18	7,82E+06	99	579	15840	7	-0,1	-1,8
Wood_adhesive	19	7,72E+06	98	360	36000			
1,2,4-butanetriol						4	-0,3	-4,1

Lignin

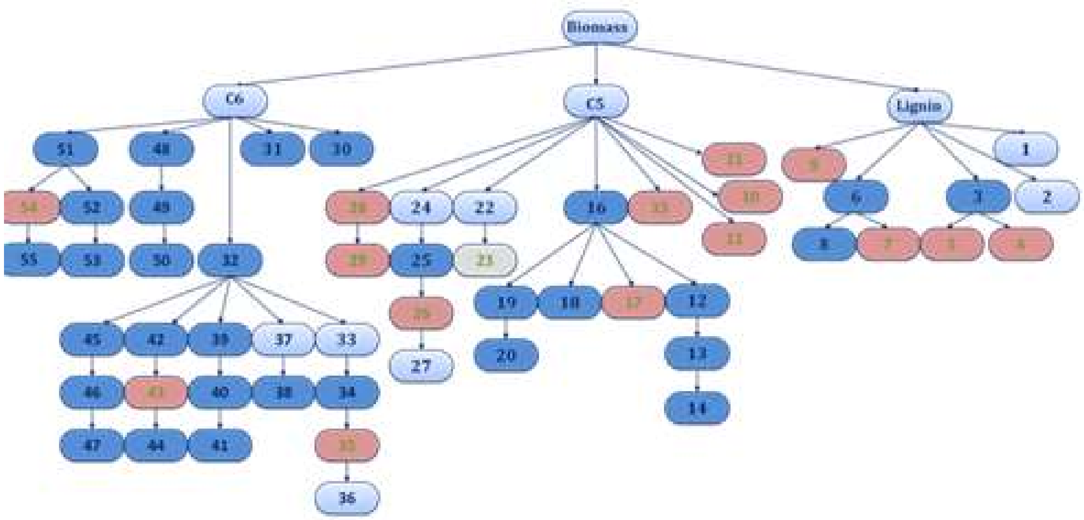
Product name	Economic: Rank (Econ)	Economic: Plant profit	Economic: Profit [%]	Economic: Price € / t	Economic: CAPACITY t / y	Greenhouse gases: Rank (GHG)	Greenhouse gases: GHG balance t CO_2 eq. / t	Greenhouse gases: Reference product t CO_2 eq. / t
Bio_PU_coatings	2	2,64E+07	117	10000	39000	4	-2,1	-2,8
Lignin_based_PF_resin	3	2,60E+07	115	1076	343980	2	-22,9	-4,2
Aromatic_polyols	4	2,31E+07	103	1620	39000			
Vanillin	5	2,29E+07	102	12000	3900		?	?
Activated_carbon	6	2,27E+07	101	2093	5742	6	-0,2	-2,4
Phenolic_oligo_monomers	6	2,27E+07	101	1076	10951			
Carbon_black	7	2,25E+07	100	835	5742	5	-0,2	-2,4
Phenolic_monomers	7	2,25E+07	100	1750	892			
Phenolic_oligomers	7	2,25E+07	100	800	5563			
Lignin as basis for PF resin						3	-3,2	-3,9
Pyrolysis oil as wood preservant						7	-0,3	-1,6
Bio_char_2	-			109		8	0,1	-0,4

- LCA extended beyond GHG
- Instead of Pareto, threshold analysis to prune value chain
- Reduction of viable paths but still DOF to explore

VALUE CHAIN ANALYSIS: SUMMARY

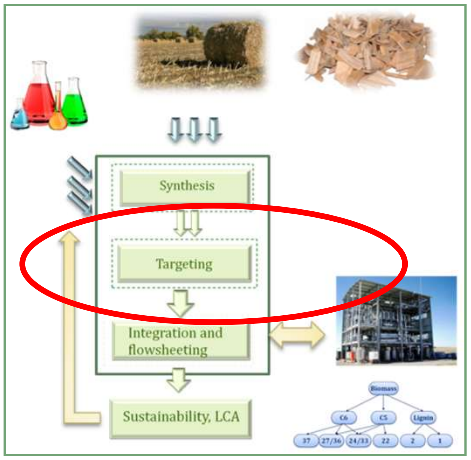


Pilots:
PUs(1), Resins(2), Xylitol (22), EtOH (24/33), PVC (27/36), Itaconate(37)



New Processes:
Pyrolysis,(3), Char (6), CB (8), Furfural (12), DFD (13), PA (14), XA (16), HGel (18), BDiol (19), BNT (20), C2H6 (25), Pulp (30), WAdeh (31), C6 (32), Cluc (39), Adip(40), PA (41), IPol (42), PP (43) ,HMF (45), 2,5-FDCA (46) ,2,5 FDCA ester (47), Pyols (48), EG (49), PEF (50), Stol (51), ISite (52), PEIF (53), SEsters (54)

Discarded:
Mmers (4), Omers (5), AC(6), Vlin (9), XOS (10), APP (15),WA (11), C5 (21), PE (17), PE (23) , IPol (28) , Deth (26), Plyne (29) SIsomers (54),



BIOREFINERY PLANT:
BUILDING INTEGRATION POTENTIAL:
BULK CHEMICALS VS. PRODUCTS

OR

TOTAL SITE ANALYSIS AS A SYNTHESIS TOOL

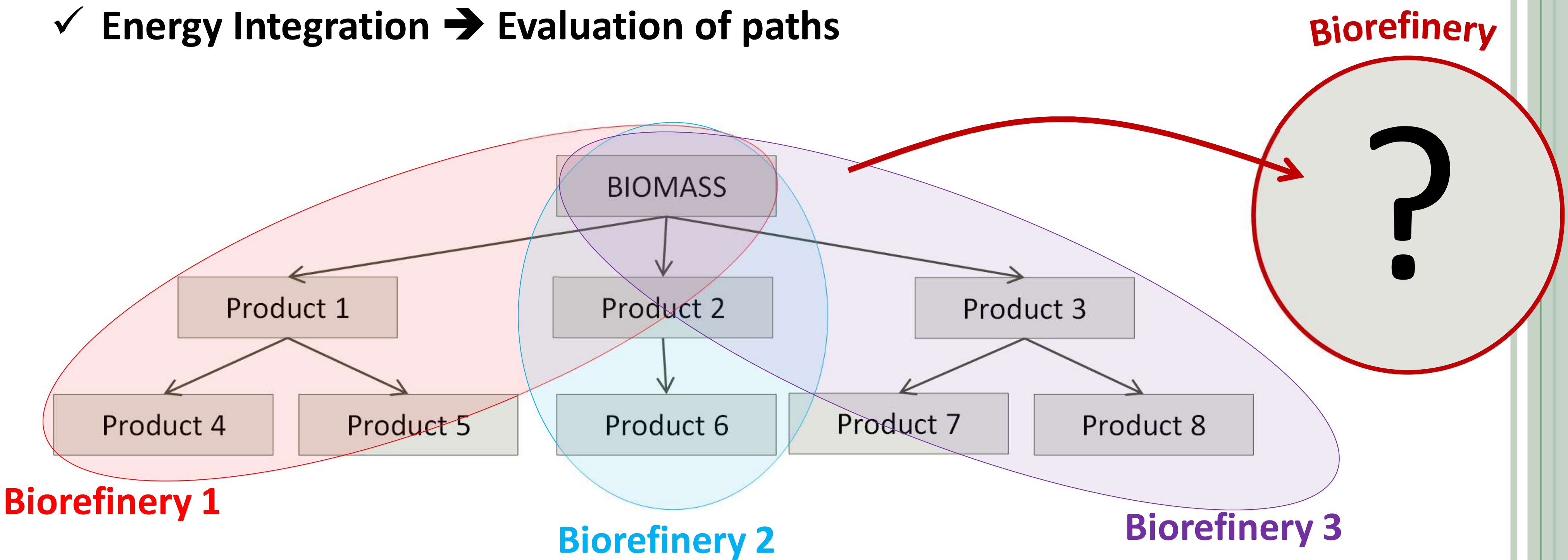
Design of integrated biorefineries

CORE PROBLEM

✓ Numerous & complex candidate paths ➔ **Synthesis problem**

✓ Different combinations ➔ Different efficiencies (optimize)

✓ **Energy Integration ➔ Evaluation of paths**



Which products portfolio subjects to MAX energy efficiencies?

Problem Description

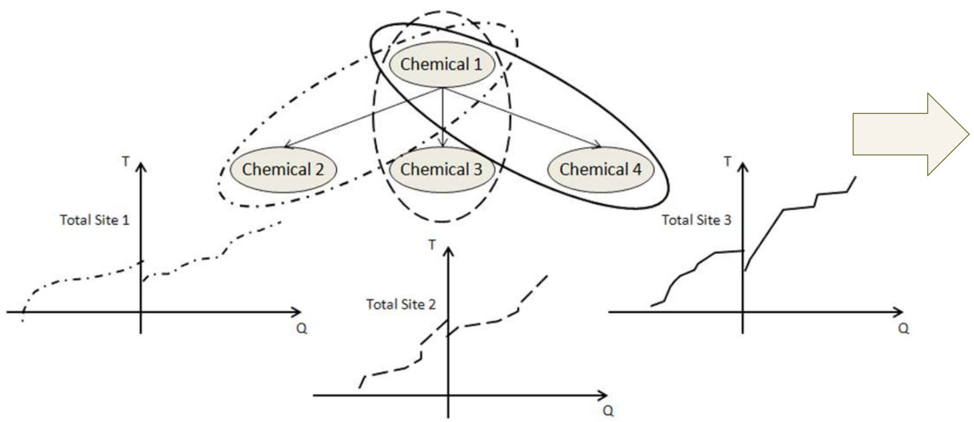
Integration

– Multi-product plants ➔ Total Site Analysis ➔ Graphically (SSSPs)

– Known processes; BUT in biorefineries: processes ≡ degrees of freedom

➢ *Total Site Analysis as process synthesis tool*

Combinatorial problem



Graphical approach: Exhaustive application

➢ Counter-productive

➢ Impractical

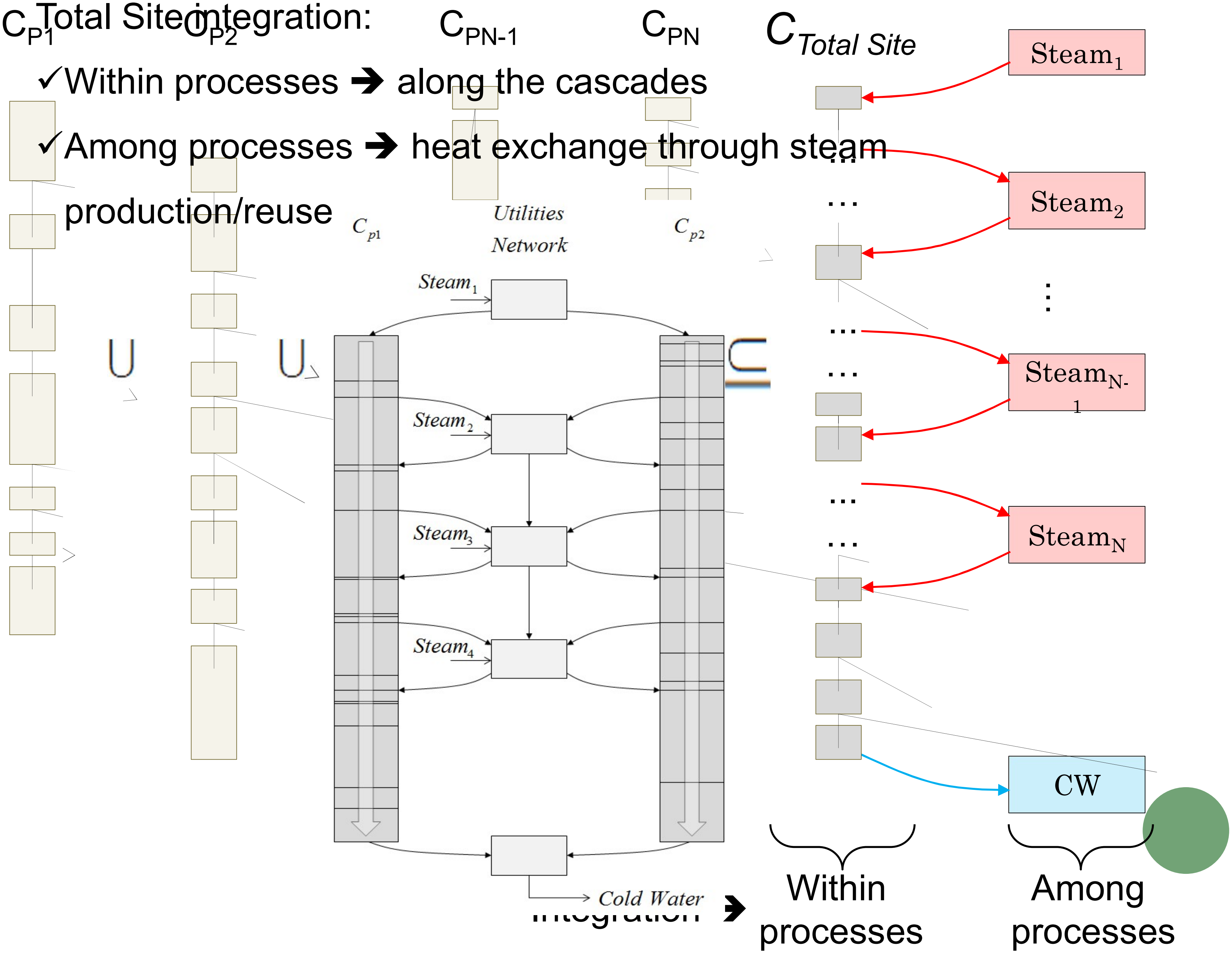
Thermodynamics with mathematical programming

- Detect promising energy synergies (within/among processes)
- Energy benefits from collocation
  - ✓ Processes that improve steam generation ?
  - ✓ Processes that optimally valorise steam ?

Total Site Cascade representation

Total Site integration:

- ✓Within processes ➔ along the cascades
- ✓Among processes ➔ heat exchange through steam production/reuse



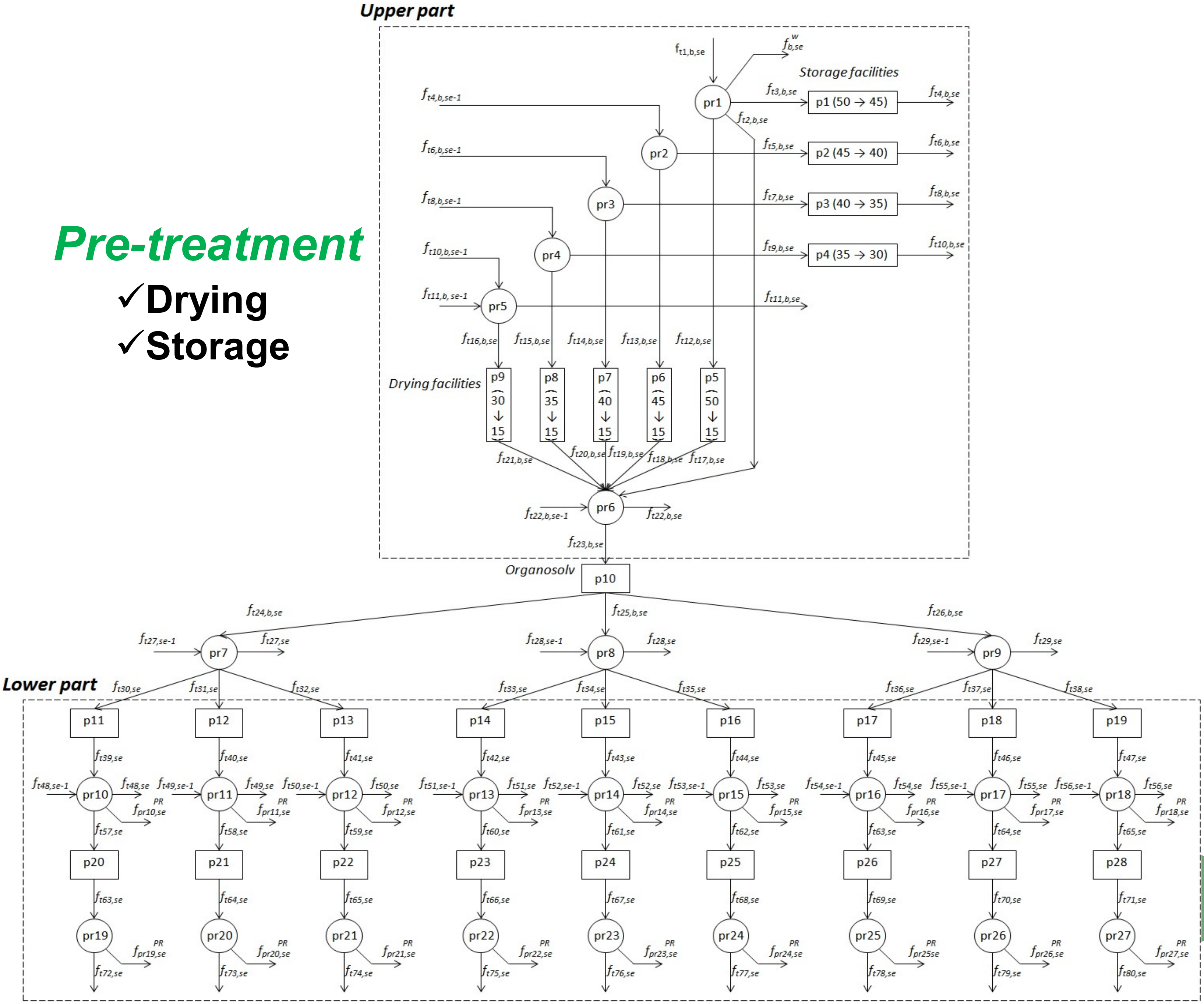
integration ➔

Extended graph : Seasonality Problem

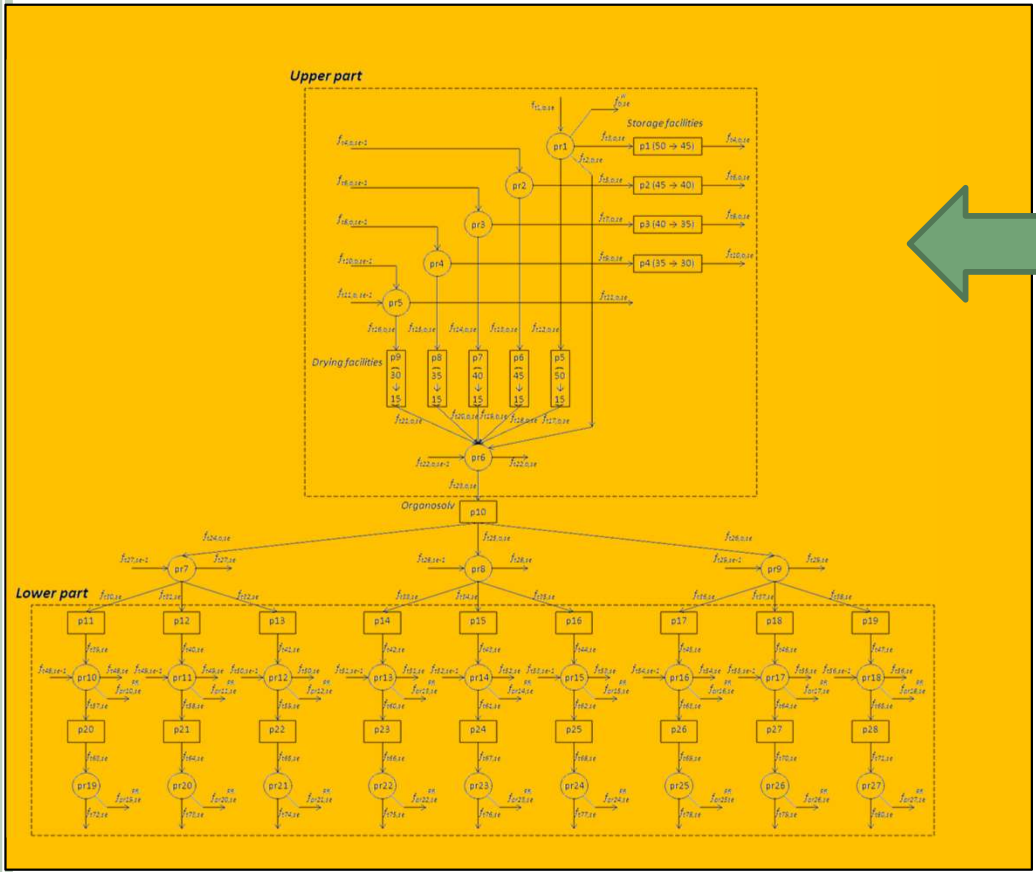
Pre-treatment

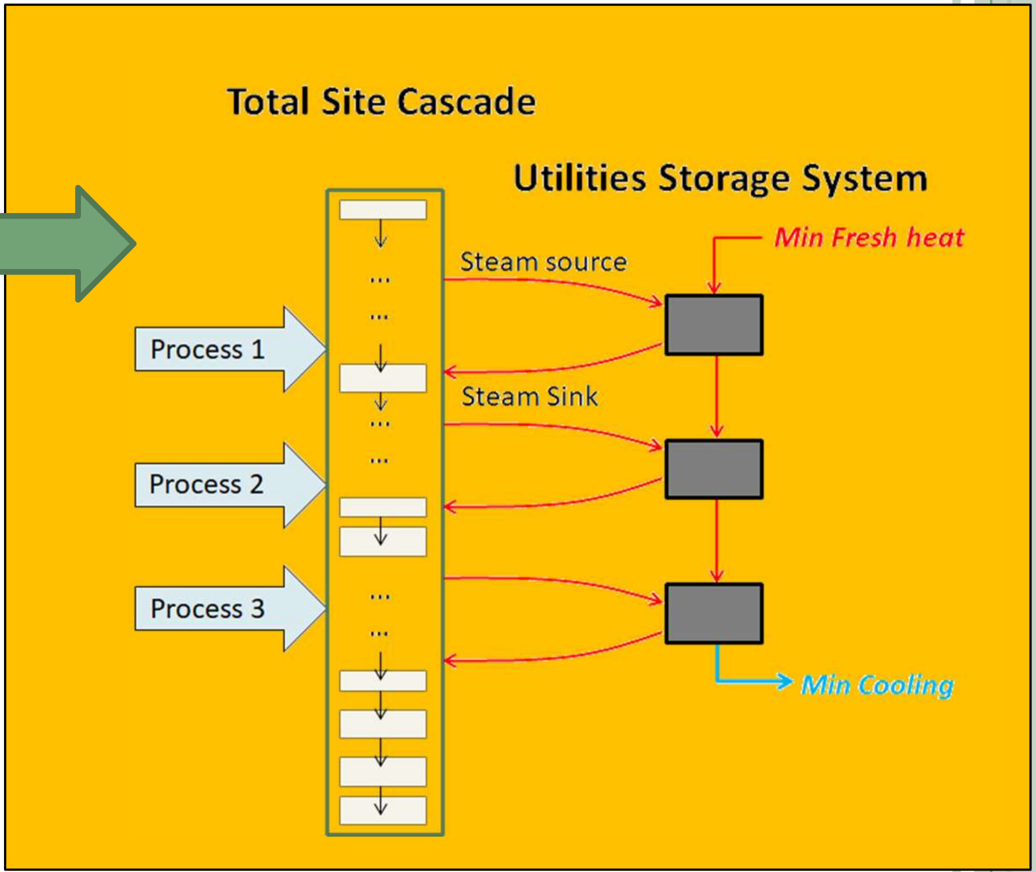
- ✓Drying
- ✓Storage

Candidate processes



Systems Representations





<u>Biorefinery Envelope</u>

- *Selection, Synthesis, Planning*
  - ✓ *Biomass varieties*
  - ✓ *Processes & Products*
  - ✓ Drying & Storage facilities network

Total Site Representation *(Cross-Interval Transshipment model)*

$$Min \qquad E^{TS}_{se} = \sum_{m\in S} c_m * Q^{TS}_{m,se} + \sum_{n\in W} c_n * Q^{TS}_{n,se}$$

$$R_{i,k,se} + \sum_{j\in CS_k} Q_{i,j,k,se} + \sum_{n\in W_k} Q_{i,n,k,se} = R_{i,k-1,se} + \Bigg[Q^H_{i,k}\cdot\Bigg(\sum_{tu\in T_p^c}$$

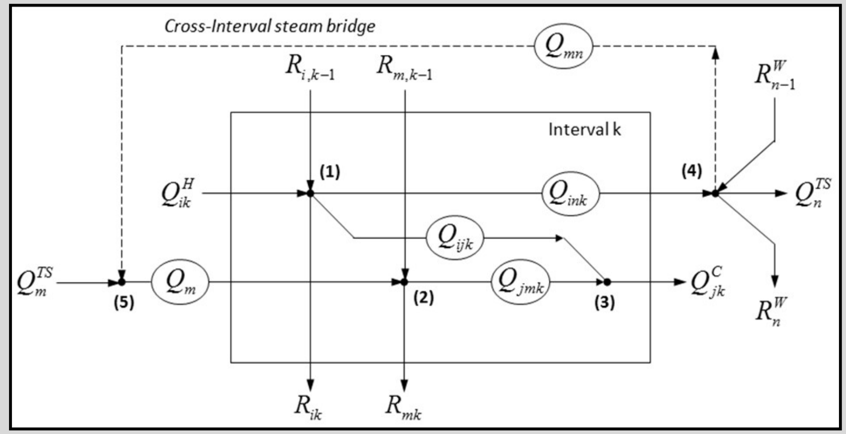
$$R_{m,k,se} + \sum_{j\in CS_k} Q_{m,j,k,se} = R_{m,k-1,se} + \sum_{m\in S_k} Q_{m',se} \qquad \forall k\in K,$$

$$\sum_{i\in HS'_k} Q_{i,j,k,se} + \sum_{m\in S'_k} Q_{m,j,k,se} = \Bigg[Q^C_{j,k}\cdot\Bigg(\sum_{tu\in T_p^{out}}\sum_{b\in B} f_{tu,b,se} +$$

$$R^W_{n-1,se} + \sum_{i\in HS'_k} Q_{i,n,k,se} = R^W_{n,se} + Q^{TS}_{n,se} + \sum_{m\in S^n} Q_{m,n,se} \qquad \forall k\in$$

$$Q^{TS}_{m,se} + \sum_{n\in W_m} Q_{m,n,se} = Q_{m,se} \qquad \forall m\in S,\ se\in SE$$

Energy balances around each C.I.T. nodes



$$Q_{m,se} \le y_m\cdot UB^S_m, \qquad \forall m\in S,\ se\in SE$$

$$\sum_{i\in H'_k} Q_{i,n,k,se} \le y_n\cdot UB^W_n, \qquad \forall k\in K,\ n\in W_k,\ se\in SE$$

$$Q^{TS}_{m,se} \le y_m\cdot UB^S_m, \qquad \forall m\in S,\ se\in SE$$

$$Q^{TS}_{n,se} \le y_n\cdot UB^W_n, \qquad \forall n\in W,\ se\in SE$$

$$\sum_{m\in S} y_m \le N^H \quad and/or \quad \sum_{n\in W} y_n \le N^C \quad and/or \quad \sum_{m\in S} y_m + \sum_{n\in W} y_n \le N^U$$

$$y_m = y_n, \qquad \forall m\in S,\ n\in W_m$$

$$R^W_{0,se} = R^W_{NW,se} = 0,\ R_{i,0,se} = R_{i,NK,se} = 0,\ R_{m,0,se} = R_{m,NK,se} = 0,$$

$$Q_{i,j,k,se} = 0\ \ \forall (i,j)\in HCS,\ k\in K,\ se\in SE$$

Selection of utilities

The Biomass Graph Representation

$$\sum_{tu \in T_{pr}^{s}} f_{tu,b,se-1} + \sum_{tu \in T_{pr}^{in}} f_{tu,b,se} = \sum_{tu \in T_{pr}^{out}} f_{tu,b,se} + \left[f_{b,se}^{w}\right]_{pr=pr1\,(fresh\ biomass)} \qquad \forall pr \in PR_{upper},\ b \in B,\ se \in SE$$

$$\sum_{tl \in T_{pr}^{s}} f_{tl,se-1} + \sum_{\substack{tu \in T_{pr}^{in} \\ b \in B}} f_{tu,b,se} = \sum_{tl \in T_{pr}^{out}} f_{tl,se} \qquad \forall pr \in I,\ se \in SE$$

$$\sum_{tl \in T_{pr}^{s}} f_{tl,se-1} + \sum_{tl \in T_{pr}^{in}} f_{tl,se} = \sum_{tl \in T_{pr}^{out}} f_{tl,se} + f_{pr,se}^{PR} \qquad \forall pr \in PR_{lower},\ se \in SE$$

$$f_{tl,se} \cdot R_p = f_{tl,se} \qquad \forall p \in P\ (p \neq organosolv),\ tl \in T_p^{in},\ tl' \in T_p^{out},\ se \in SE$$

- **Mass balances around**
  - ✓ **Product nodes**
  - ✓ **Process units**

$$IC_p \leq y_p \cdot UB_t^{f} \qquad \forall p \in P$$

$$IC_p \geq y_p \cdot LB_t^{f} \qquad \forall p \in P\ (p \geq \text{"p10"})$$

$$D_p \cdot IC_p \leq \sum_{b \in B} f_{tu,b,se} \qquad \forall p \in P\ (p = organosolv),\ tu \in T_p^{in},\ se \in SE$$

$$IC_p \geq \sum_{b \in B} f_{tu,b,se} \qquad \forall p \in P,\ tu \in T_p^{in},\ se \in SE$$

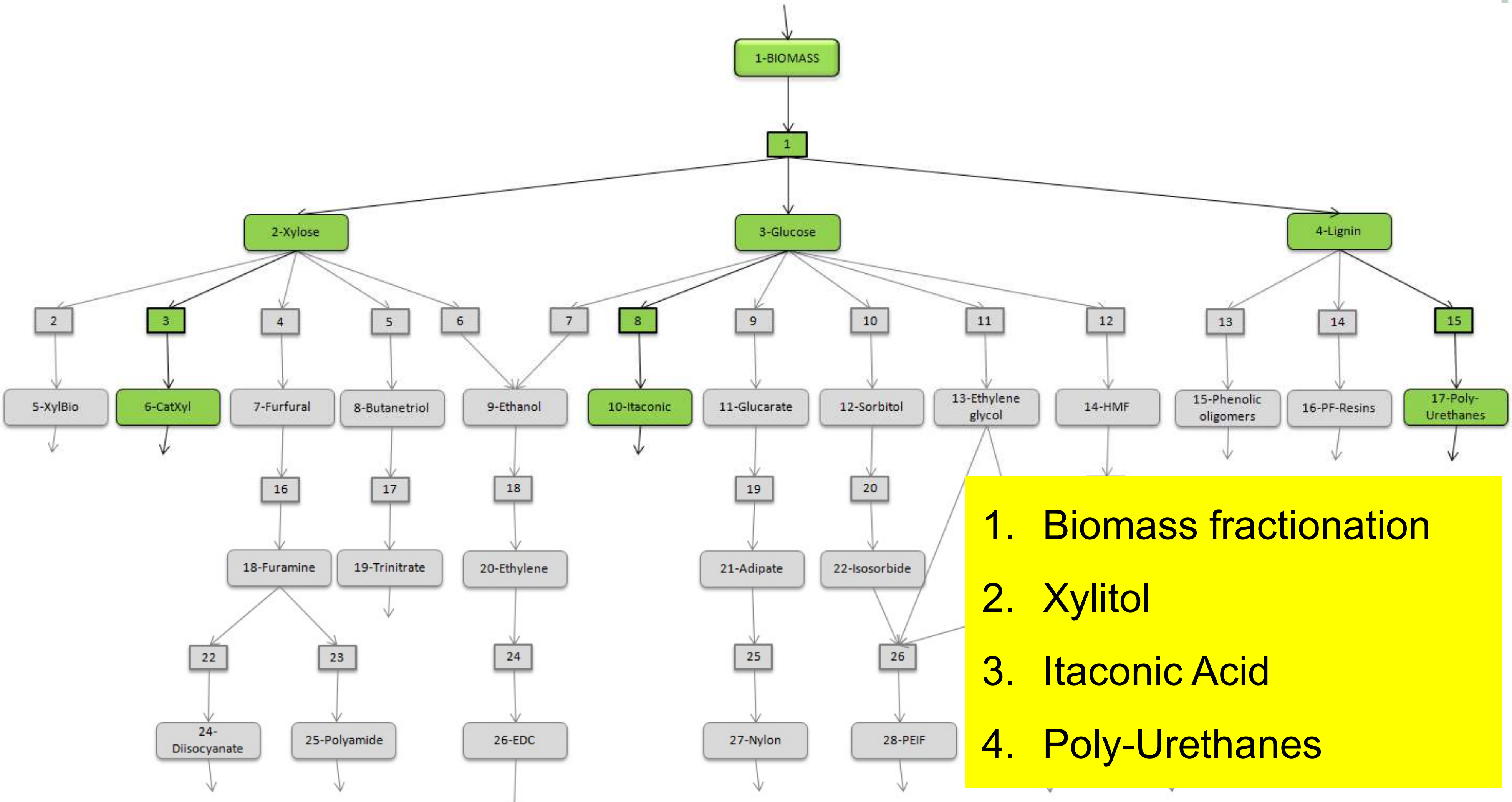
$$\sum_{t \in T_p^{in}} F_{t,se} \leq IC_p \qquad \forall p \in P,\ se \in SE$$

$$\sum_{t \in T_p^{in}} F_{t,se} \geq IC_p \cdot (1 - D_p) \qquad \forall p \in P,\ se \in SE$$

$$\sum_{t \in T_{pr}^{s}} f_{tu,b,se1-1} = \sum_{t \in T_{pr}^{s}} f_{tu,b,se4} \qquad \forall pr \in PR_{upper},\ b \in B$$

- ✓ **Manage fluctuations**
- ✓ **Storing over seasons**

Best portfolio

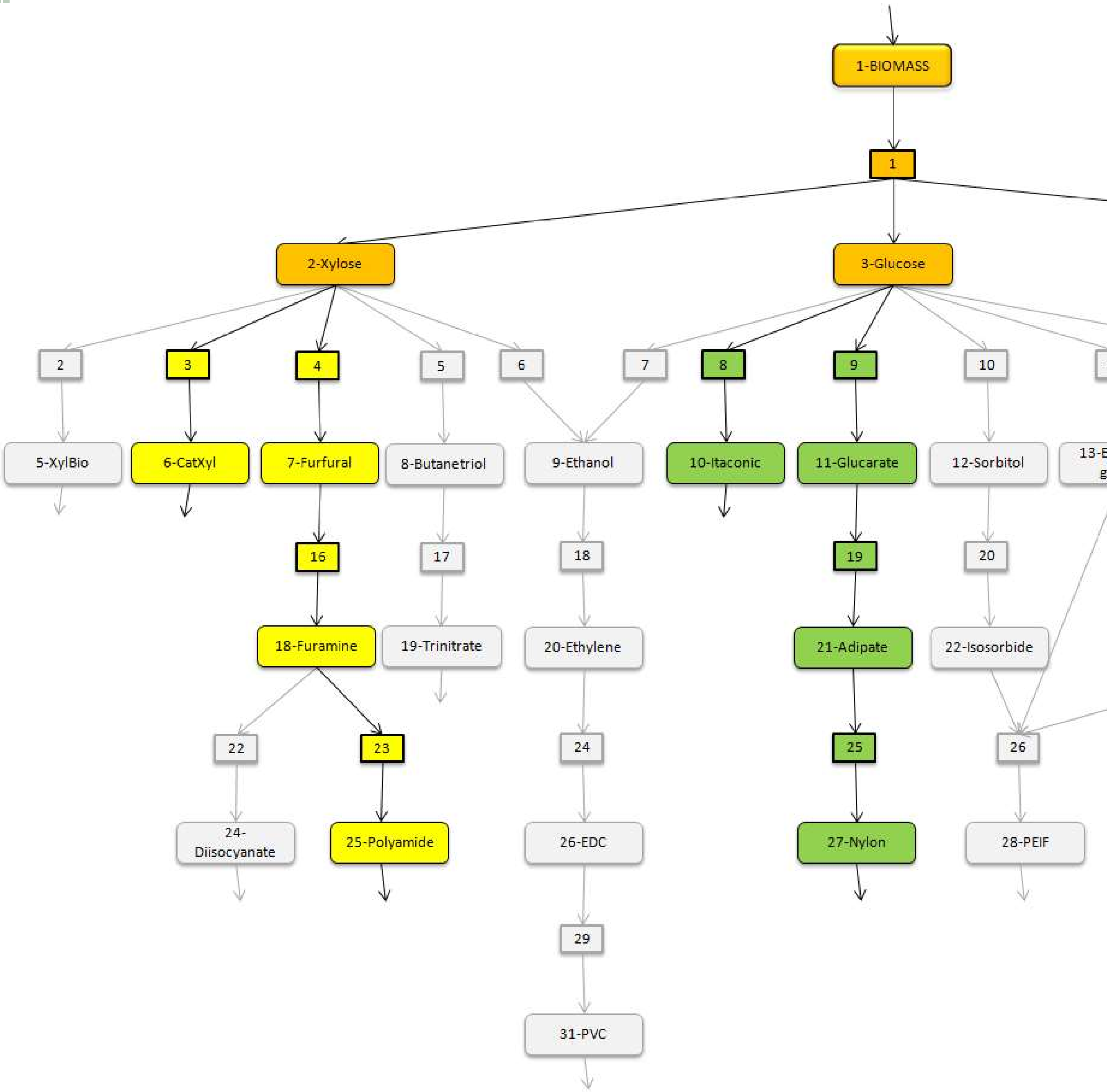


1. Biomass fractionation
2. Xylitol
3. Itaconic Acid
4. Poly-Urethanes

	Before Integration	Total Site	Savings
Steam [MW]	157	54	66%
Cooling [MW]	173	70	60%
Energy Cost [Meuro/yr]	13	4,3	67%

Energy promising portfolios

Integer Cut: Top 10 solutions



Top portfolios include:

1. Xylitol
2. Itaconic Acid
3. Nylon
4. Resins
5. Poly-Urethanes

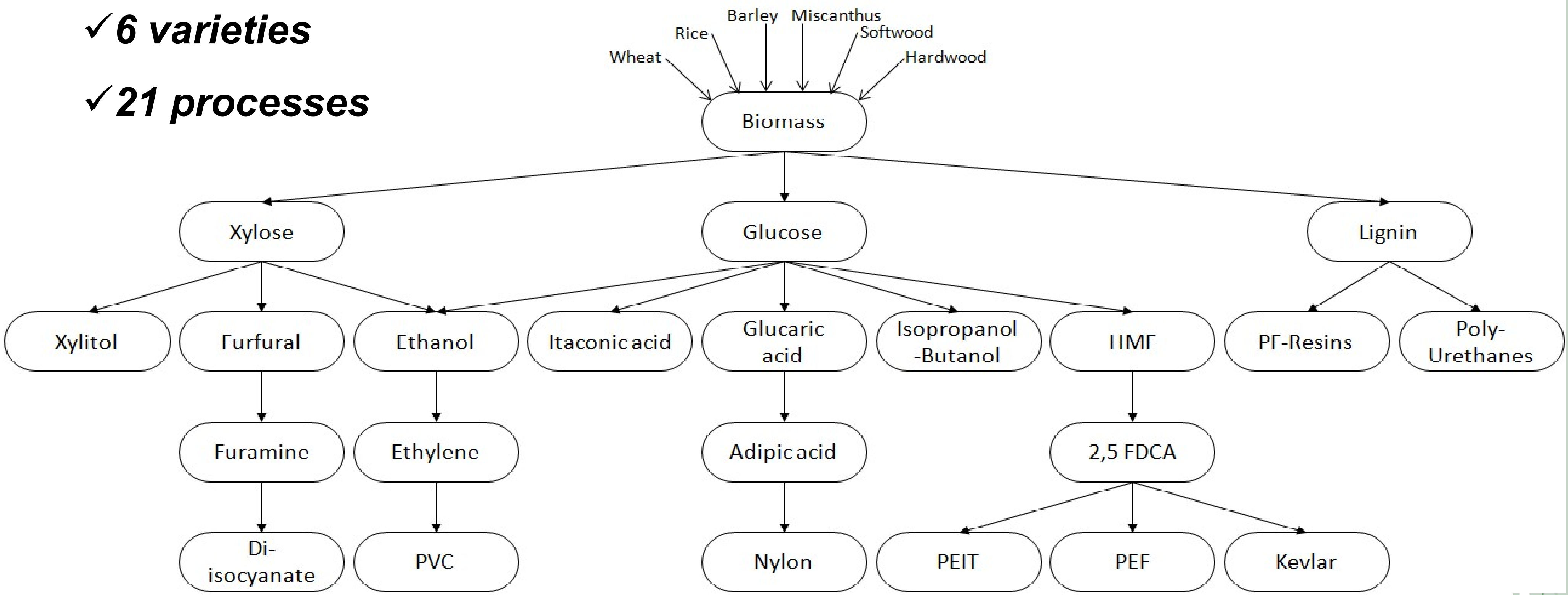
Energy Savings:
50%-70%

THE INTEGRATED APPROACH TO MULTIPLE FEEDSTOCK: SCHEDULING, PLANNING AND SAFETY

Six-feedstock plant

Value Chain

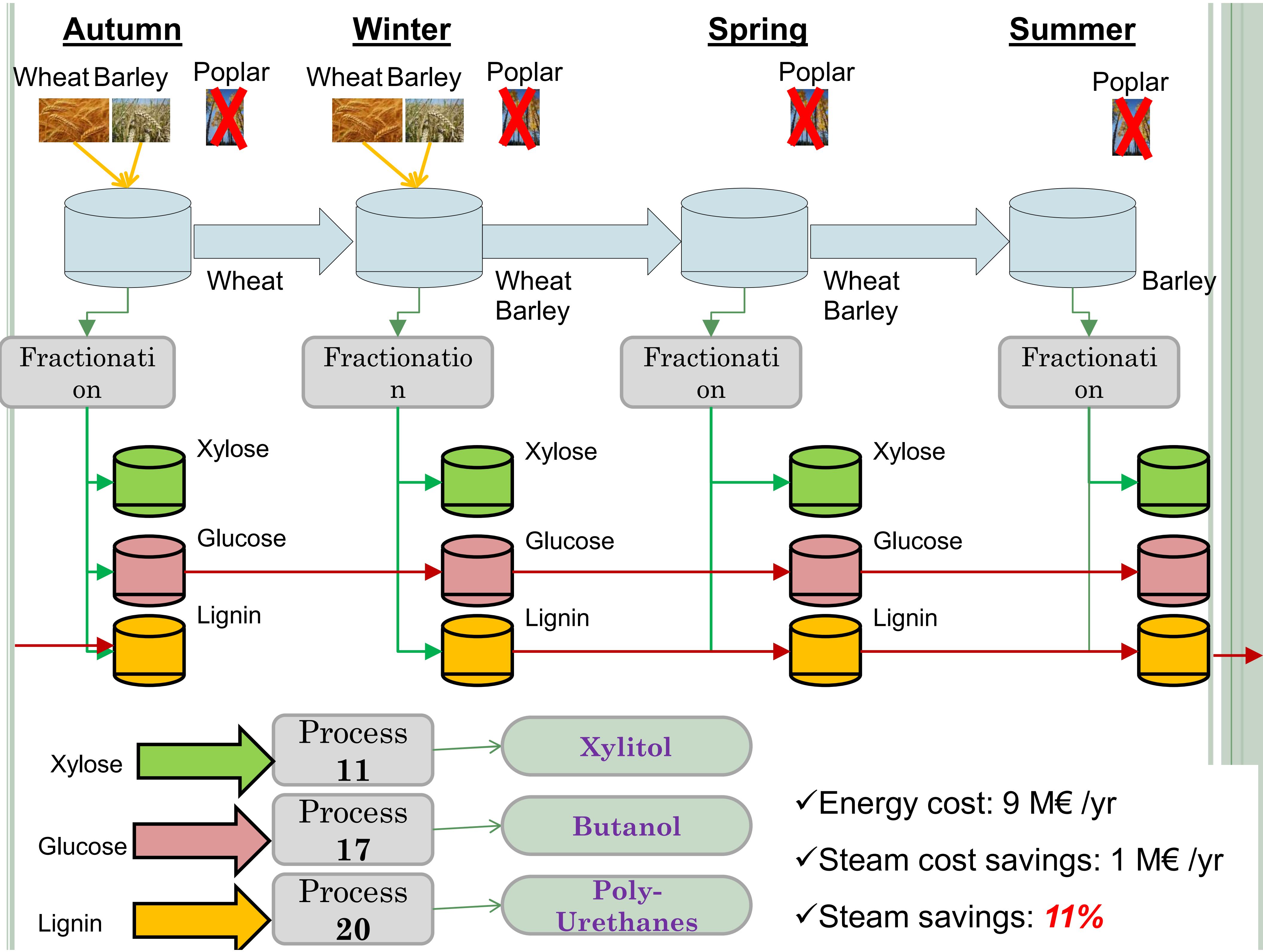
- ***6 varieties***
- ***21 processes***



Studies:

1. ***Hungary Seasonality***
2. ***Preference of varieties***

Season	Wheat [kg/hr]	Barley [kg/hr]	Poplar [kg/hr]
Winter	79,700	15,900	23,400
Spring	900	6,900	23,400
Summer	0		23,400
Autumn	0		23,400



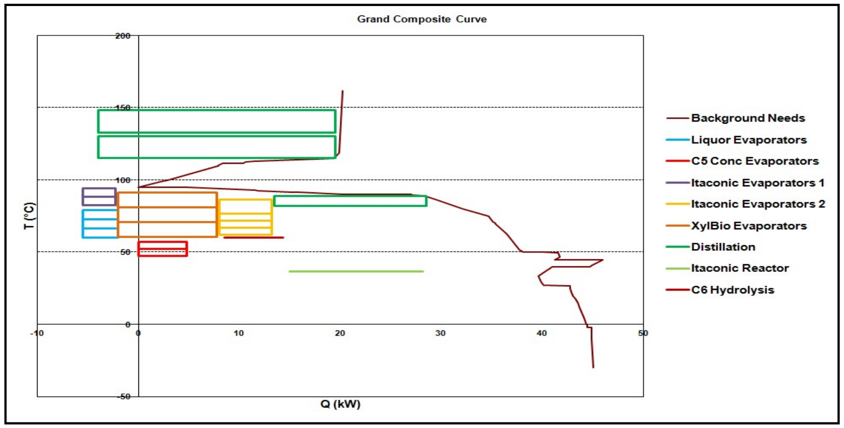
✓Energy cost: 9 M€ /yr

✓Steam cost savings: 1 M€ /yr

✓Steam savings: *11%*

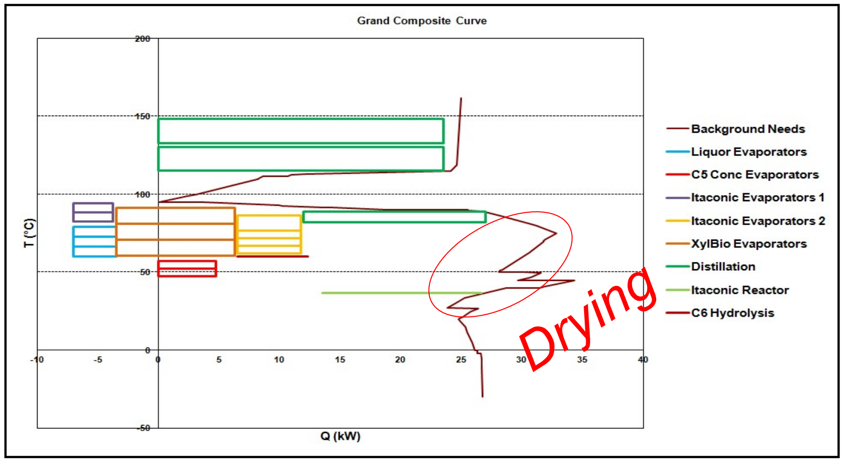
CHANGE-OVERS IN OPERATION

Rice



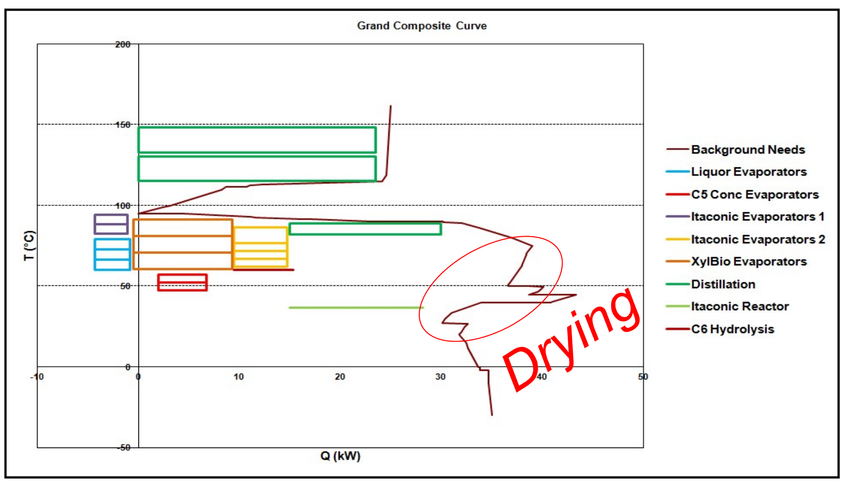
	Before PI	After PI	Recovery
Hot Utilities MW	235	28	88 %
Cold Utilities MW	130	38	71 %

Poplar



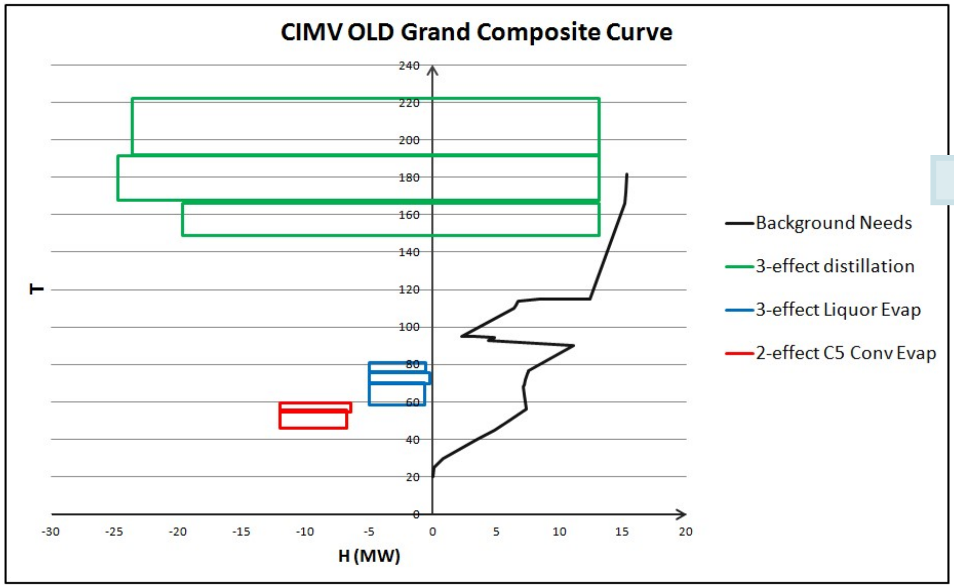
	Before PI	After PI	Recovery
Hot Utilities MW	284	36	88 %
Cold Utilities MW	157	19	88 %

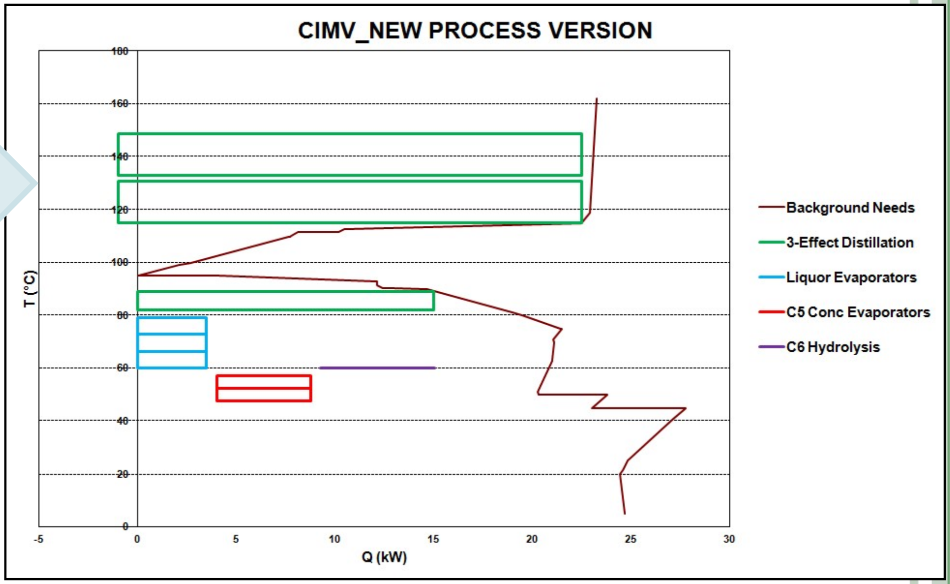
Birch



	Before PI	After PI	Recovery
Hot Utilities MW	289	30	90 %
Cold Utilities MW	149	25	83 %

TRADE-OFFS WITH SAFETY



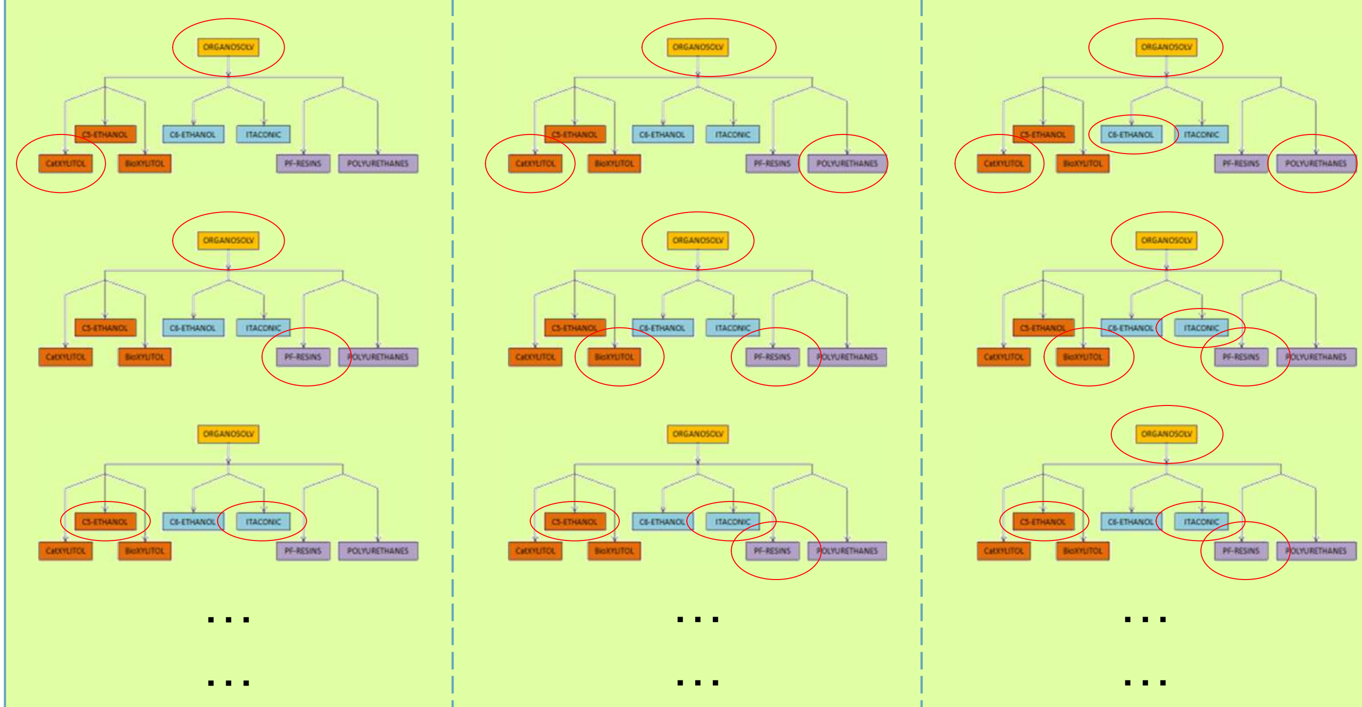


1. Higher Background needs
2. Trade-off with higher integration potential for distillation

Old CIMV:	***New CIMV version:***
Q_hot_{min} = 38 MW	**Q_hot_{min} = 24 MW (37% less consumption)**
Q_cold_{min} = 23 MW	**Q_cold_{min} = 19 MW (17% less consumption)**

SAVINGS VS VALUE CHAIN SIZE

2 Processes included	3 Processes included	4 Processes included



Ranges of Energy Savings		
17 – 86 %	***21 – 86 %***	***64 – 84 %***

- It matters a lot what you choose:
  - choice matters more as the number of products is smaller
- Optimization and thermodynamics have to dance together

AN INTEGRATED APPROACH TO INCLUDE WASTE VALORIZATION AND TREATMENT

INDICATIVE PROBLEM SIZE

Liquid wastes:

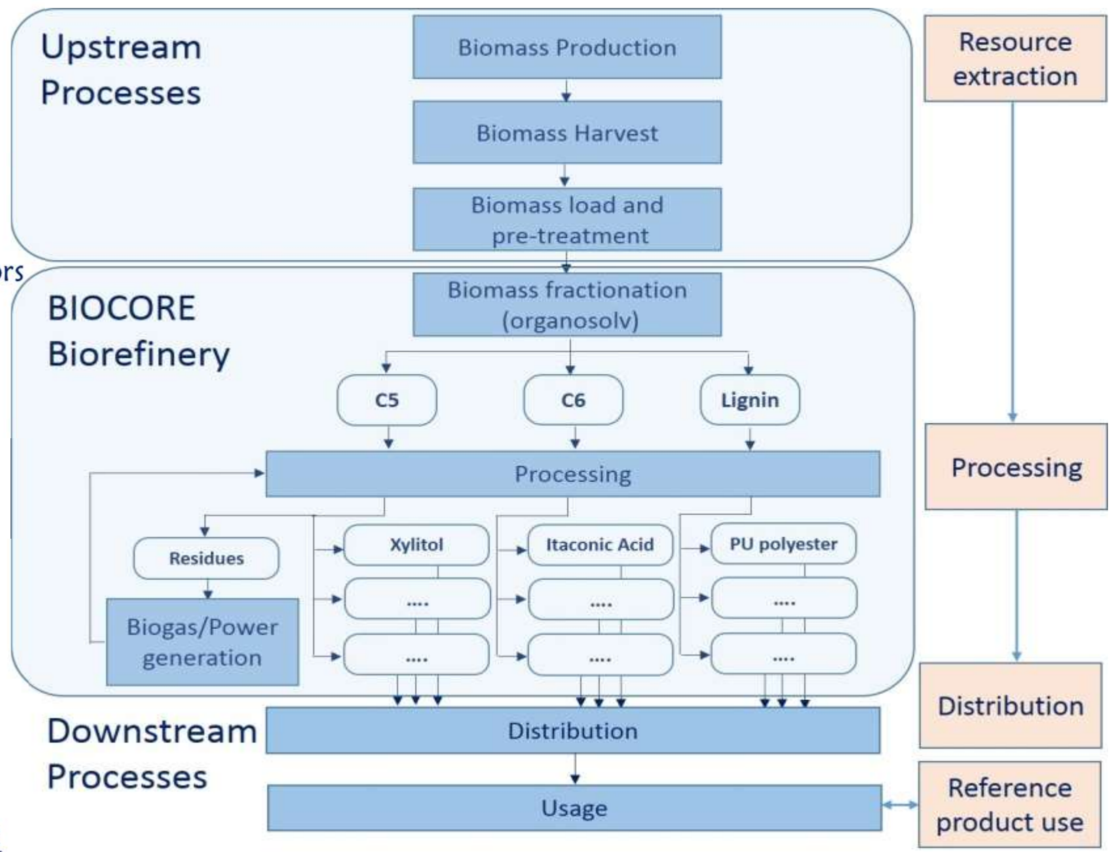
- Anaerobic Digestion
- Activated Sludge
- Trickling Filters
- Rotating Biological Conductors
- Aerated Lagoon
- Stabilization Pond

Liquid Reuse:

- Reverse Osmosis
- Micro-filtration

Catalyst Regeneration:

- Chemical Precipitation
- Ion Exchange



Solid wastes:

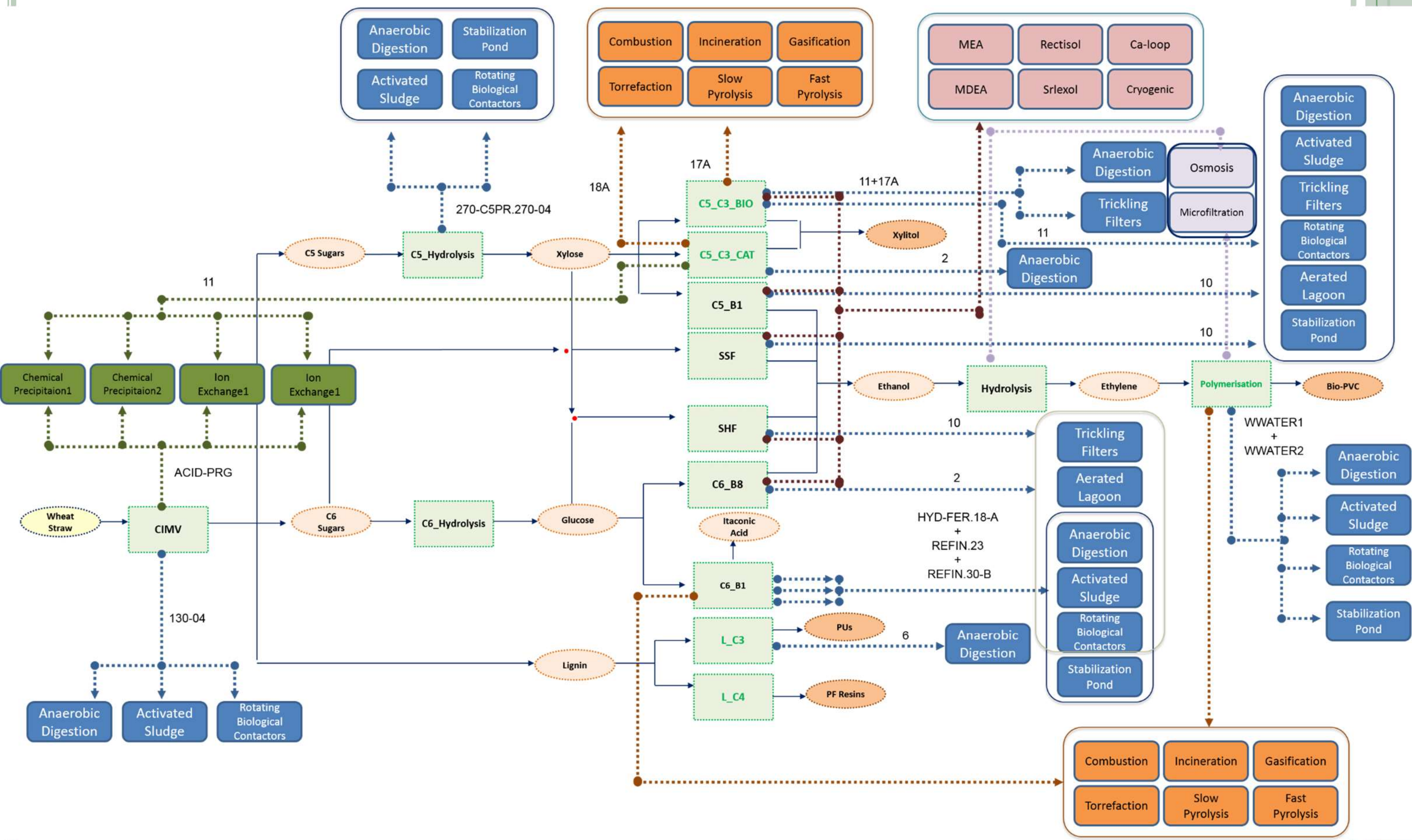
- Combustion
- Incineration
- Gasification
- Torrefaction
- Slow Pyrolysis
- Fast Pyrolysis

Gaseous Emissions:

- Chemical Absorption: MEA / MDEA
- Physical Absorption: Rectisol/ Selexol
- Ca-loop
- Membrane Reactors
- Cryogenic Methods

A total of 49 waste streams produced need to be classified and properly treated

SYSTEM SUPERSTRUCTURE



DECENTRALIZED TREATMENT – IMPROVEMENTS WITH THE SYSTEMS APPROACH

Scenario: Grassroots design: Xylitol, C6 Ethanol, & PU

	Liquid 1	Liquid 2	Liquid 3	Liquid 8	Liquid 11
Technology	RBC	RBC	RBC	AD	AD
Fixed Cost*		0.185		4.722	
			4.907		
Energy Cost*		0.172		-	-
			0.172		
Revenue*	-	-		-	0.845
			0.845		
Total Cost*			4.234		

	Liquid 1	Liquid 2	Liquid 3	Liquid 8		Liquid 11
Technology	RBC	SP	SP	SP	AD	AD
Fixed Cost*	0.139		0.029			0.136
			0.304			
Energy Cost*		0.129			-	
			0.129			
Revenue*	-	-				0.013
			0.013			
Total Cost*			0.420			

Up to 2 new technologies

- Cost: 4 million $/year

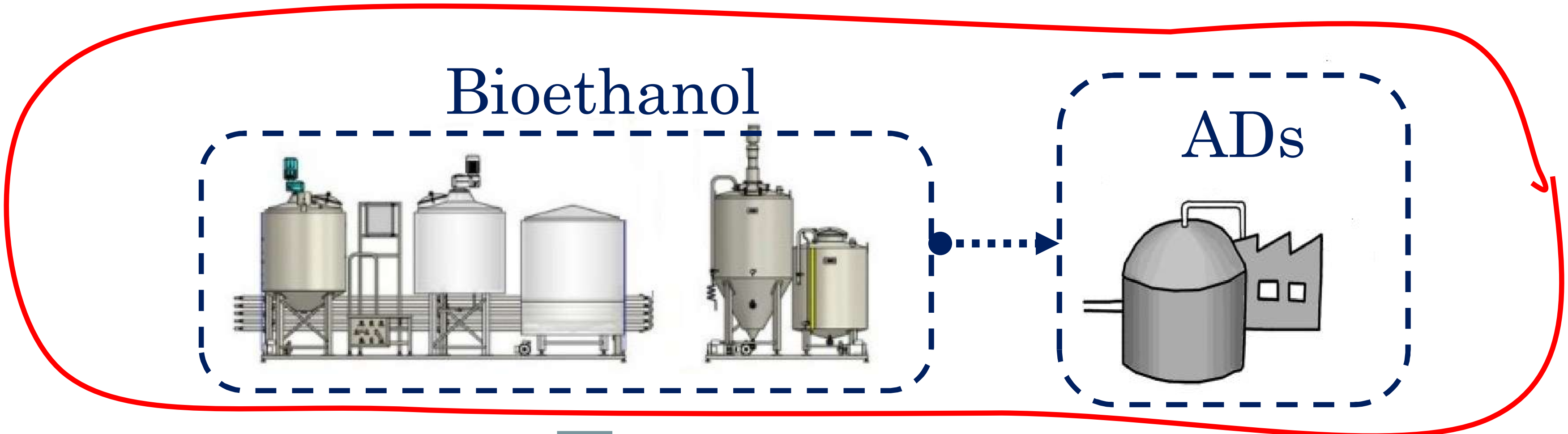
No limit

- Cost: 0.4 million $/year

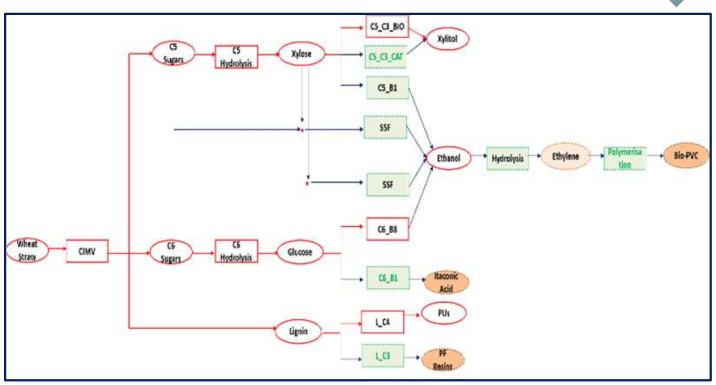
*million $/year

RETROFITTING

An existing one product refinery with a small waste treatment



Towards a multi-product Biorefinery



What about the waste streams?

+

How to use the existing AD unit?

INTEGRATION OVERTURNS TRADE-OFFS

N ≤2

	Liquid 1	Liquid8	Liquid 1+2+3+8+11
Technology	RBC	SP	ADs
Fixed Cost*	0.082	0.025	0
		0.107	
Energy Cost*	0.077		-
Revenue*			1.225
Total Cost*		-1.040	

Profit 1,040 million $/year

- Two additional technologies can integrate nicely with the existing AD to save capital

*million $/year

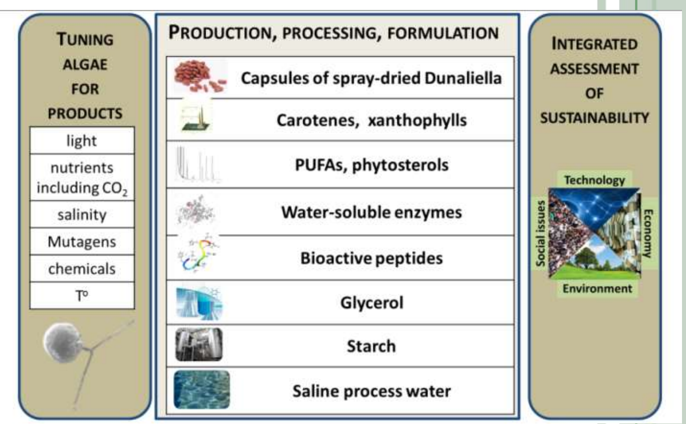
SHIFTING TOWARDS 2G AND 3G PLANTS

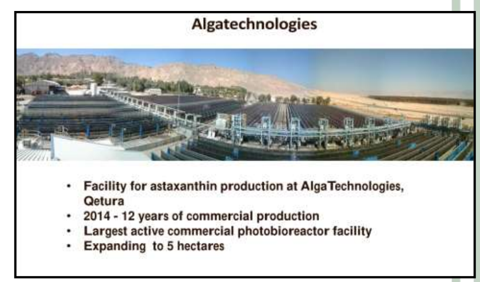
- ALGAL PLANTS

- WASTE AS A RENEWABLE RESOURCE

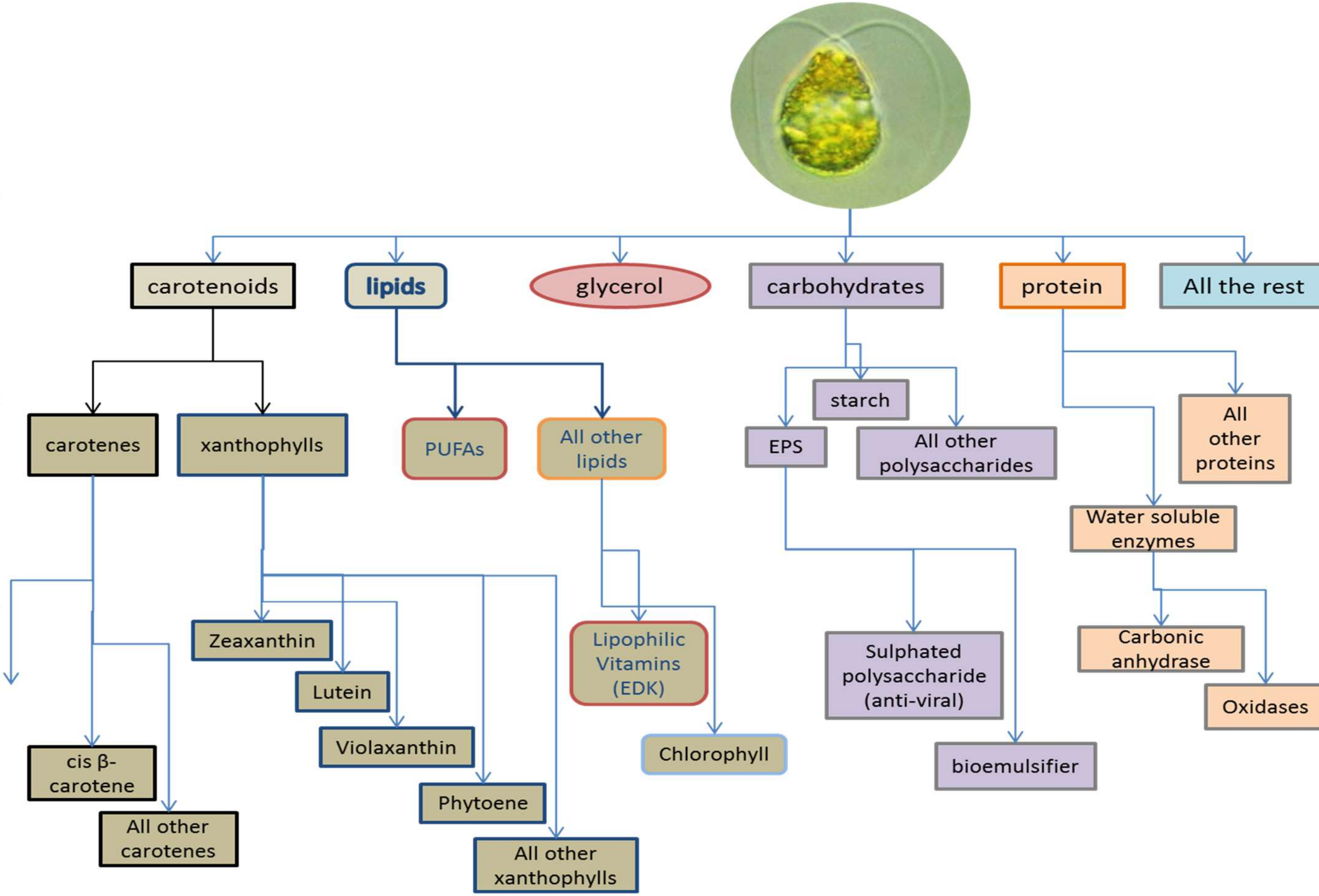
Algae – developments in Europe

- Water access and the occasional sunshine
- Emphasis on fuel production remains limited; much more promising lines on specialty chemicals (fuels can be a by product)
- Dependence on specialties
  - Significant options in DSP
  - Seasonal production
  - Plant flexibility is crucial and essential





METHODOLOGY ON NEW APPLICATIONS: ALGO-BIOREFINERIES



MICROALGA BIOREFINERY

Cultivation

- Open ponds
- Closed systems
- Feed of CO_2, water and nutrients
- Sunlight
- Mixing (paddle wheels)

Harvesting & processing

- Centrifugation in combination with other harvesting technologies
- Accumulation of fractions in the cells

Fraction extraction

- Mixtures of chemicals with common properties in the fractions
- Competitive chemistries among fractions

Product recovery

- Unique thermodynamic properties
- Advanced separation processes
- Pure chemicals or mixtures

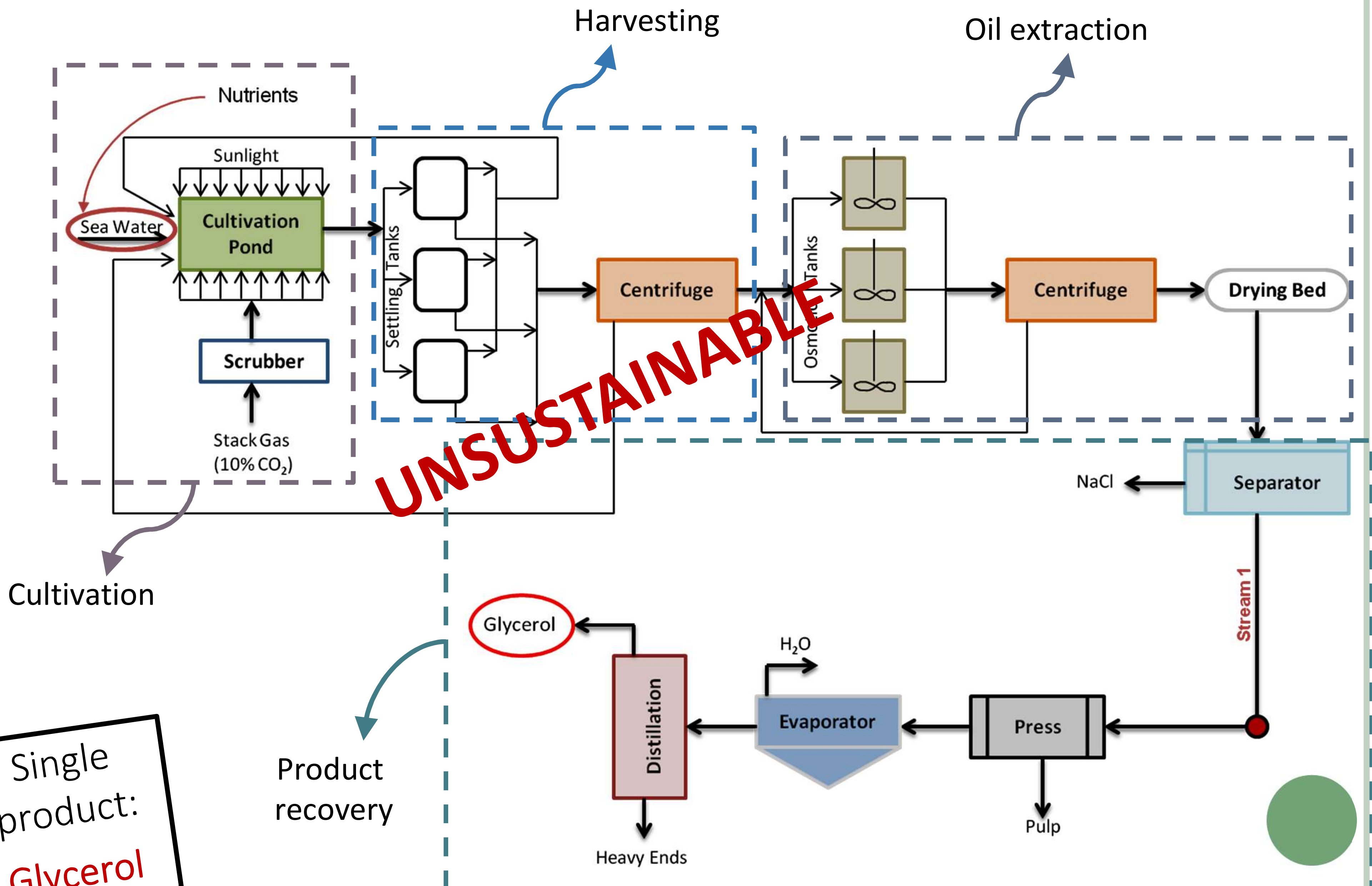
Selection of product portfolios: how about a straightforward evolutionary approach?

… Start with a product (one of your choice)

… Evolve the design to incorporate additional products

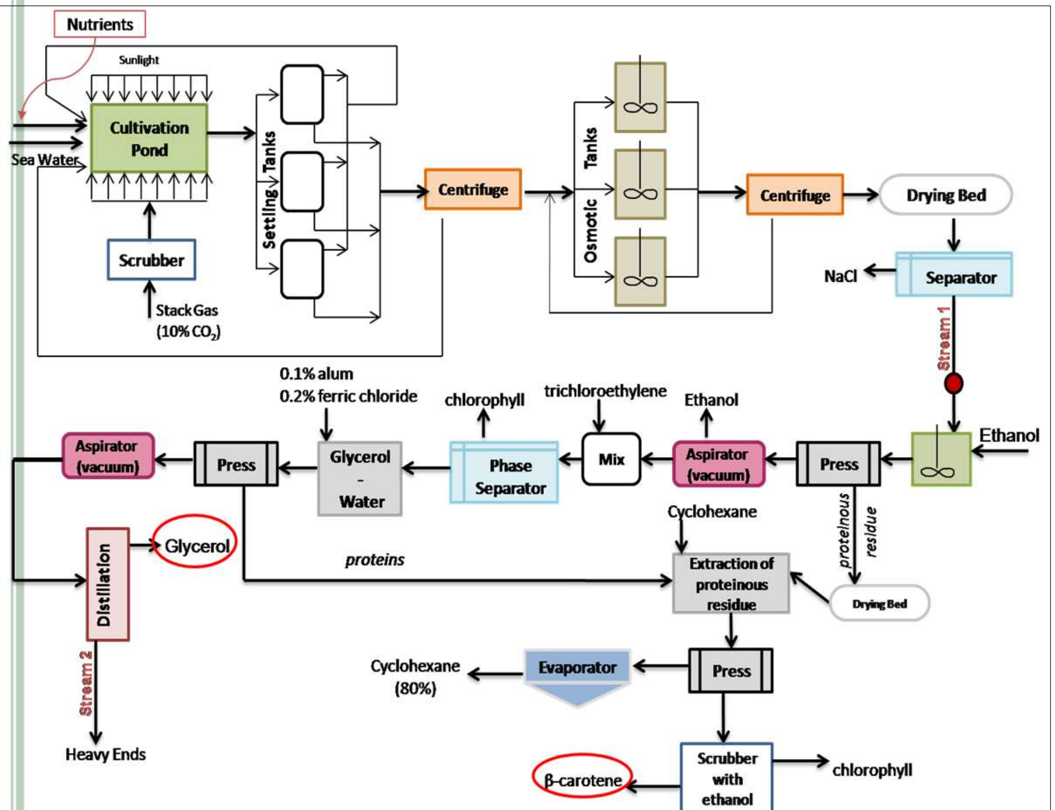
… Continue this way, step-by-step, towards a multiproduct biorefinery

SINGLE PRODUCT STARTUP

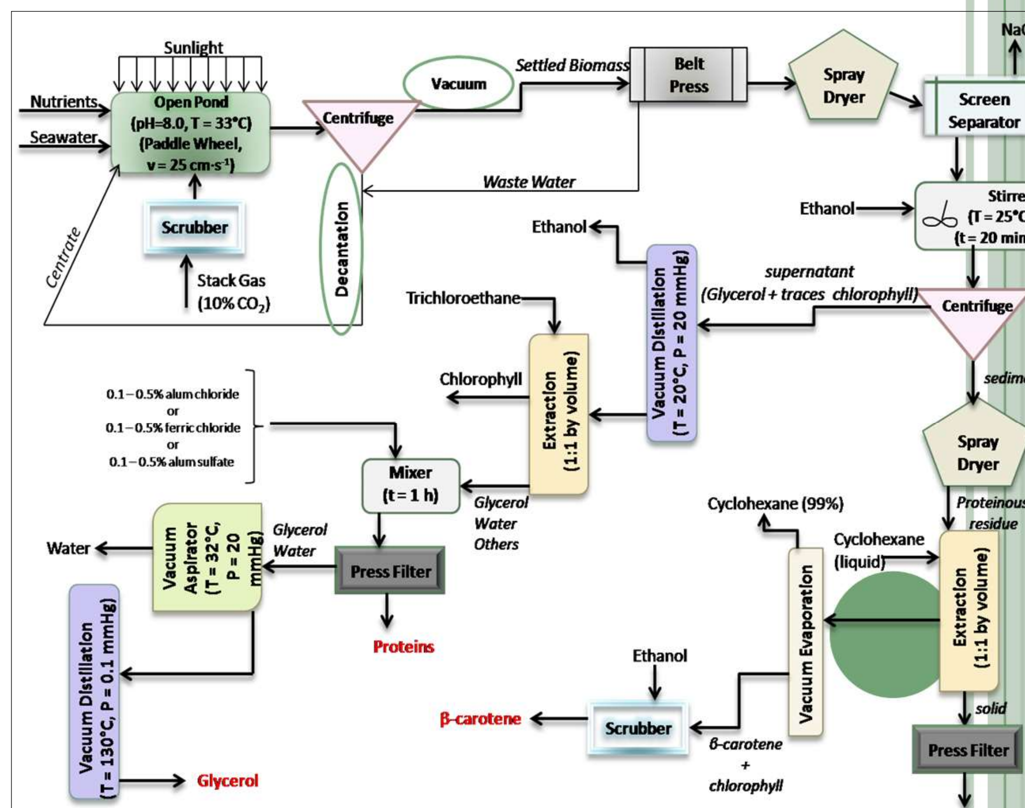


Single product: Glycerol

Introduce new product: β-carotene



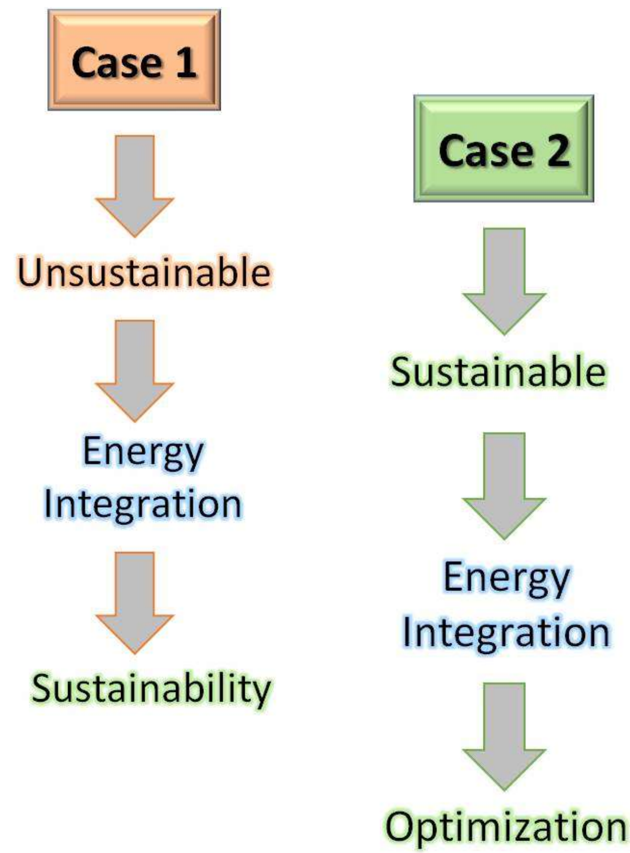
- Conditions in osmotic tanks do not favor co-production.
- Settling tanks are redundant.



- Scope to replace spray dryers and belt press
- Provided that protein meal is used as food supplement (e.g. fishmeal), solvents have to be replaced

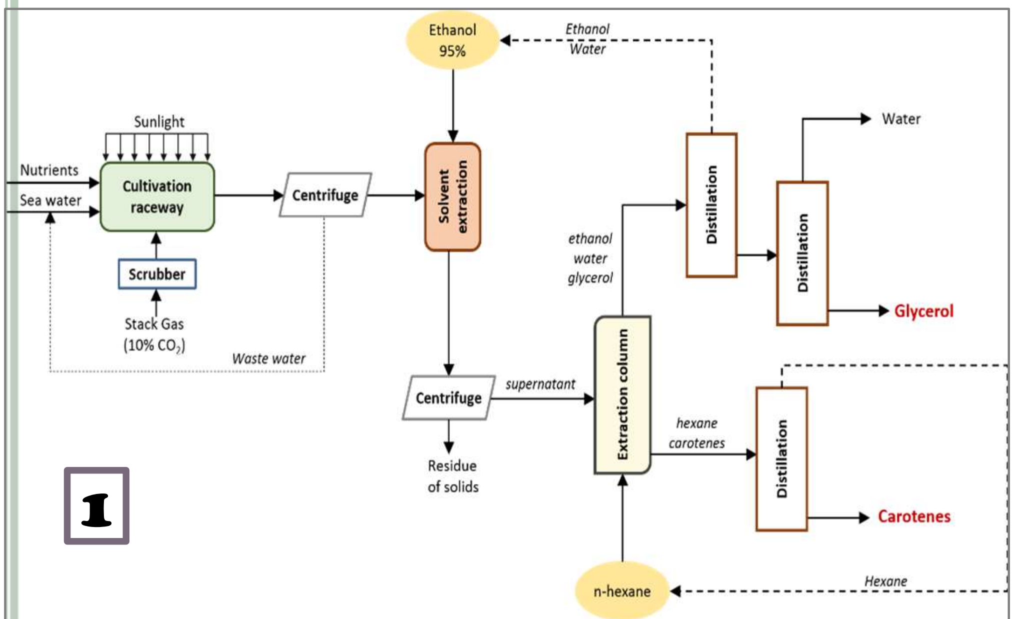
New result: excellent but process engineering changes are too many…

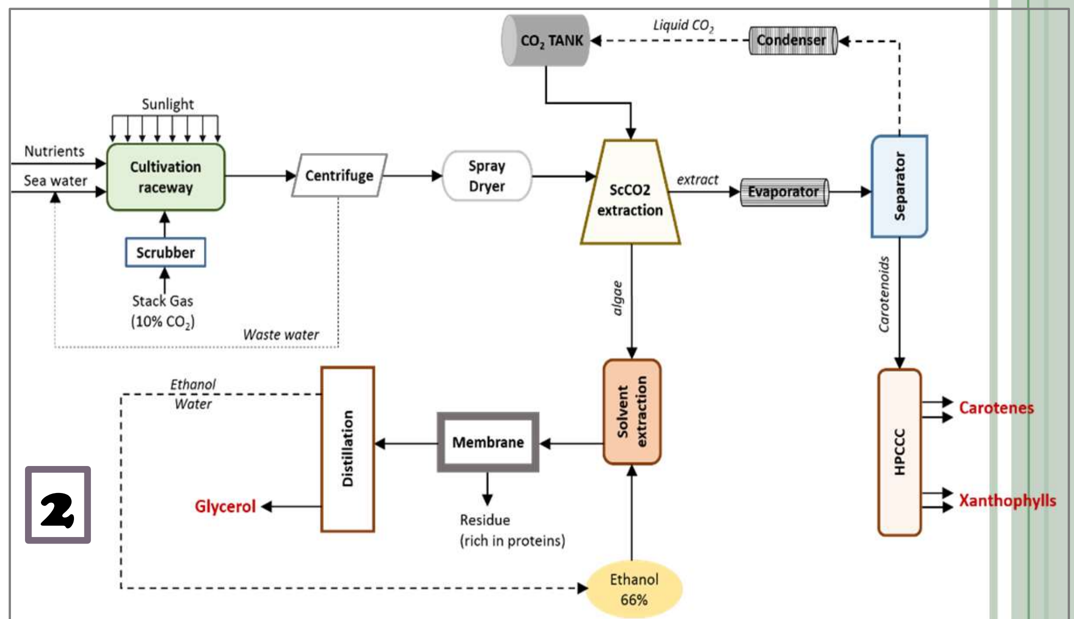
Annual cost ($)	*Case 1*	*Case 2*
Solvents	**4,800**	**10,300**
Ethanol	4,800	5,900
Hexane	—	4,400
Energy	**50,228**	**275,301**
Distillation	50,228	275,301
Feed	**21,800**	**40,900**
Nutrients	12,900	32,000
Dunaliella	8,900	8,900
Products	**63,400**	**18,762,000**
Glycerol	63,400	63,400
β-carotene	—	18,699,000
Profit/Loss ($/yr)	**-13,400**	**18,436,000**

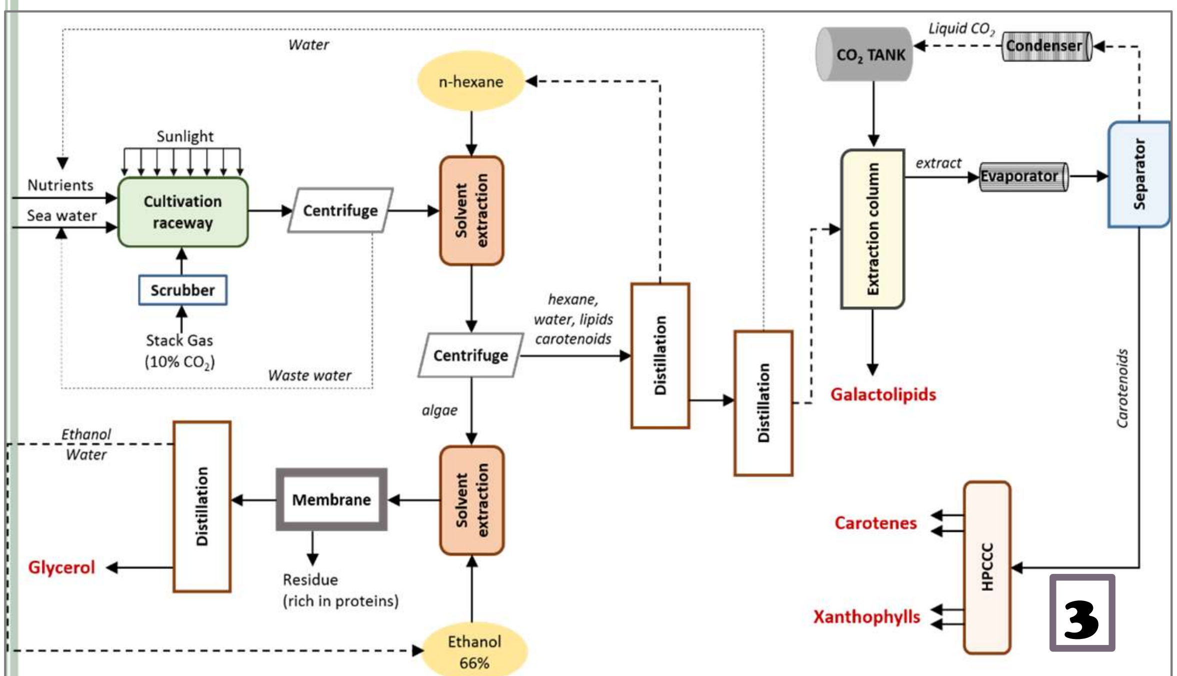


- Venture is profitable but integration scheme is very different
- Retrofitting the first scheme to the second is not economical

INTRODUCING NEW PRODUCTS







1 Glycerol, carotenes mixture

2 Glycerol, pure carotenes, pure xanthophylls

3 Glycerol, pure carotenes, pure xanthophylls, galactolipids

The evolutionary approach to process development could turn into a free fall to the Death Valley

Towards a systematic approach

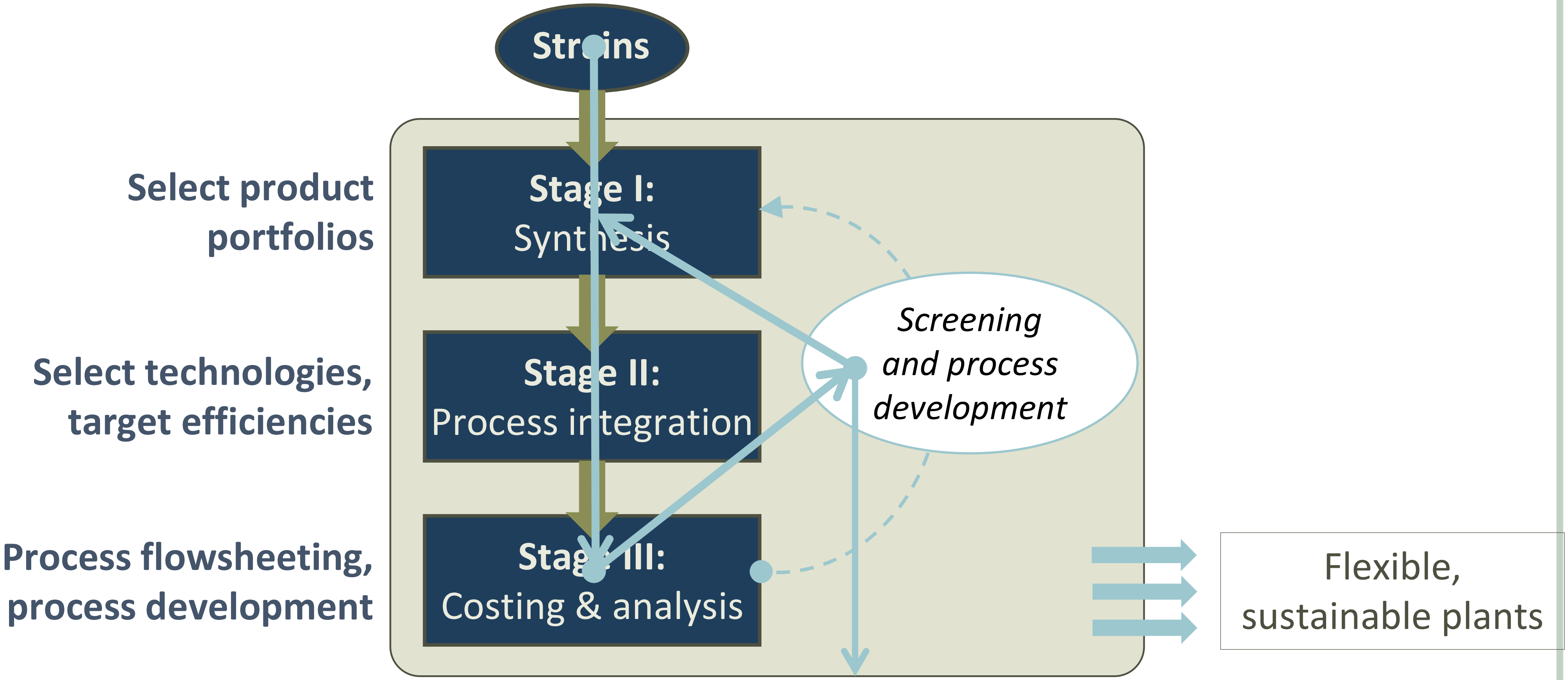
… Combine state-of-the-art of systems engineering (synthesis, process integration, advanced flowsheeting..)

… Capitalize on advanced modelling and optimization

… Possible to generalize and scale-up into very large problems

… Algal plants HAVE to be FLEXIBLE in order to survive

STEPS OF THE SYSTEMS METHODOLOGY



- High-throughput screening
- Could address uncertainty analysis
- User interaction with decision-support process

D-FACTORY OPTIONS

Feedstock

- Dunaliella

Processes

- Ultrafiltration
- Nanofiltration
- Ethanol extraction
- Hexane extraction
- $ScCO_2$ extraction
- H_2O extraction
- Chromatography
- …

Products

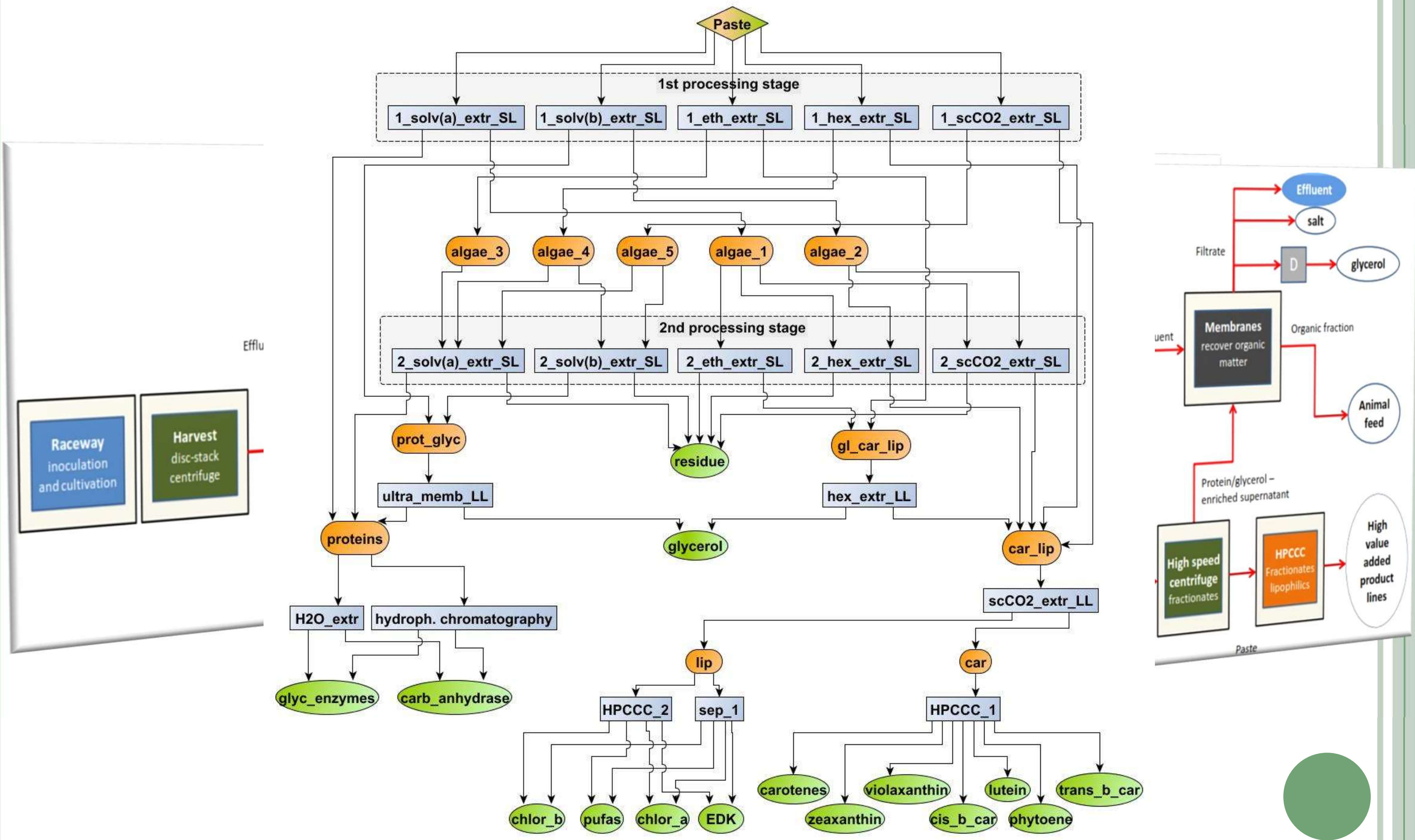
- Glycerol
- Cis-b-carotene
  Trans-b-carotene
- Zeaxanthin
  Violaxanthin
- Phytoene
  Lutein
- Chlorophyll a
  Chlorophyll b
- PUFAs
  EDK vitamins
- Glycerol enzymes
  Carbonic anhydrase

Carotenoids

Lipids

Proteins

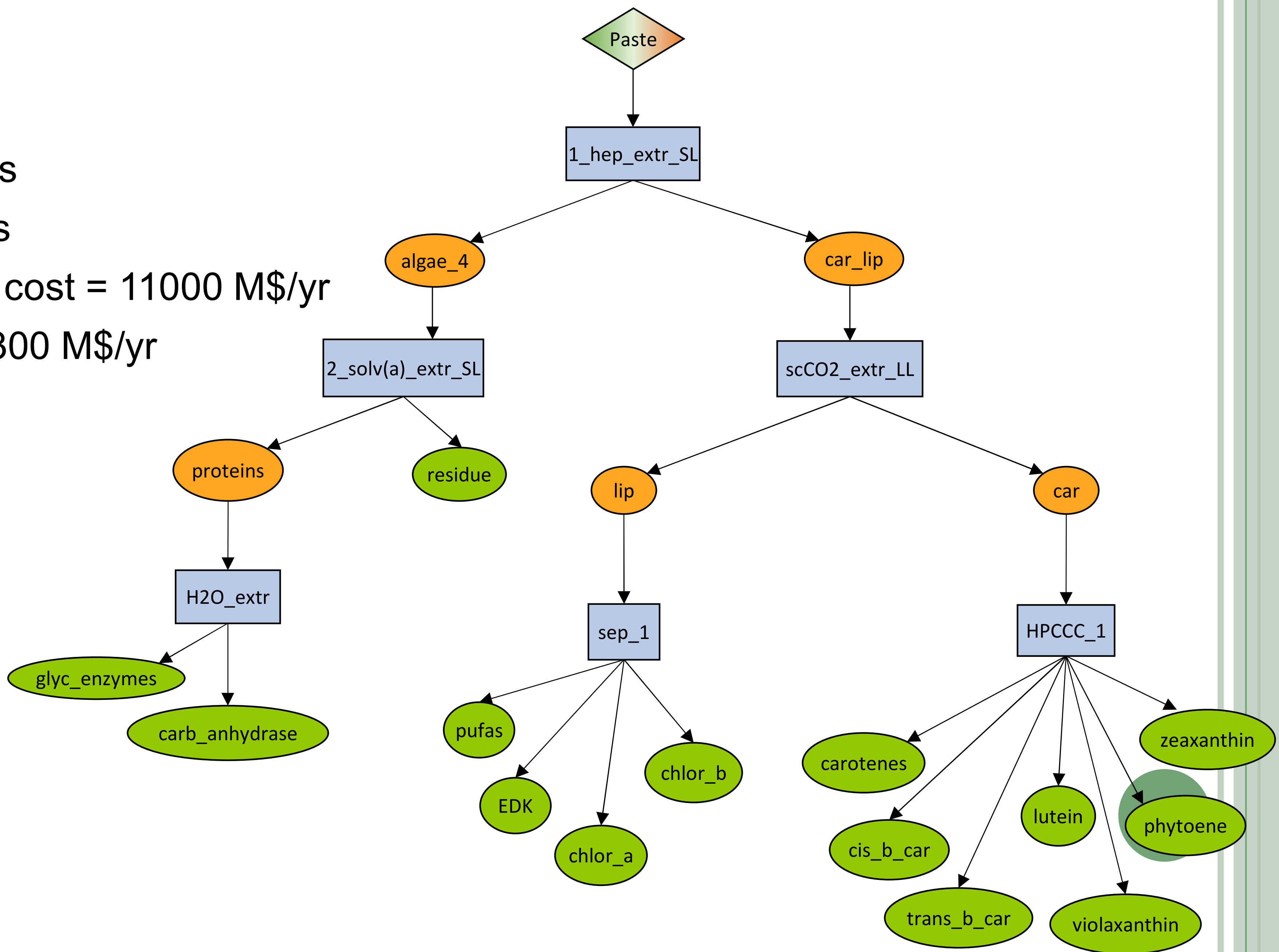
Building the screening model…



… AND OPTIMIZING VALUE CHAIN AND TECHNOLOGY SELECTION

Best solution

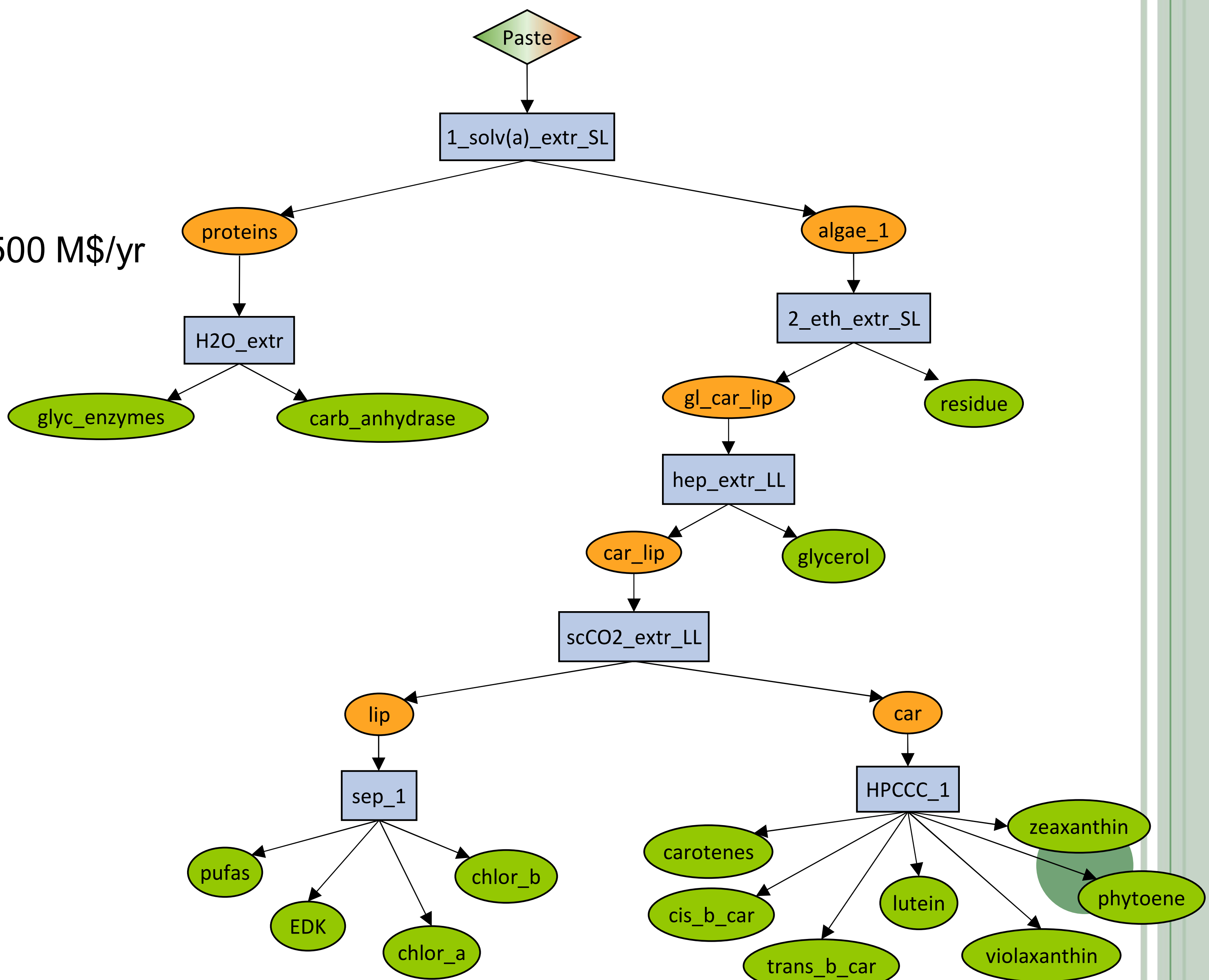
- 6 processes
- 13 products
- Equipment cost = 11000 M$/yr
- Profit = 87300 M$/yr



… POINTING TO BACKUP OPTIONS

<u>Best solution including glycerol</u>

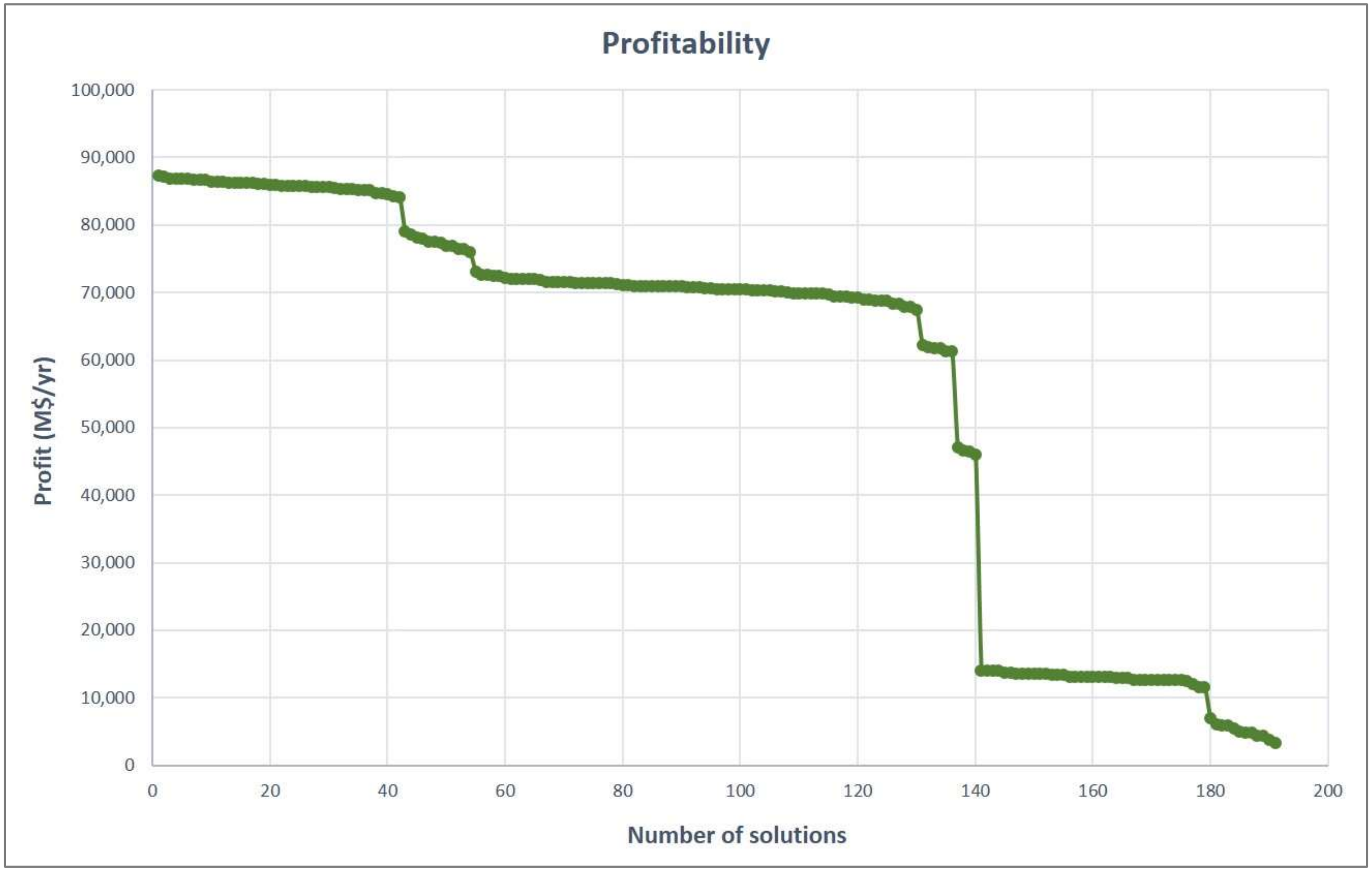
- 7 processes
- 14 products
- Equipment cost = 11500 M$/yr
- Profit = 86600 M$/yr



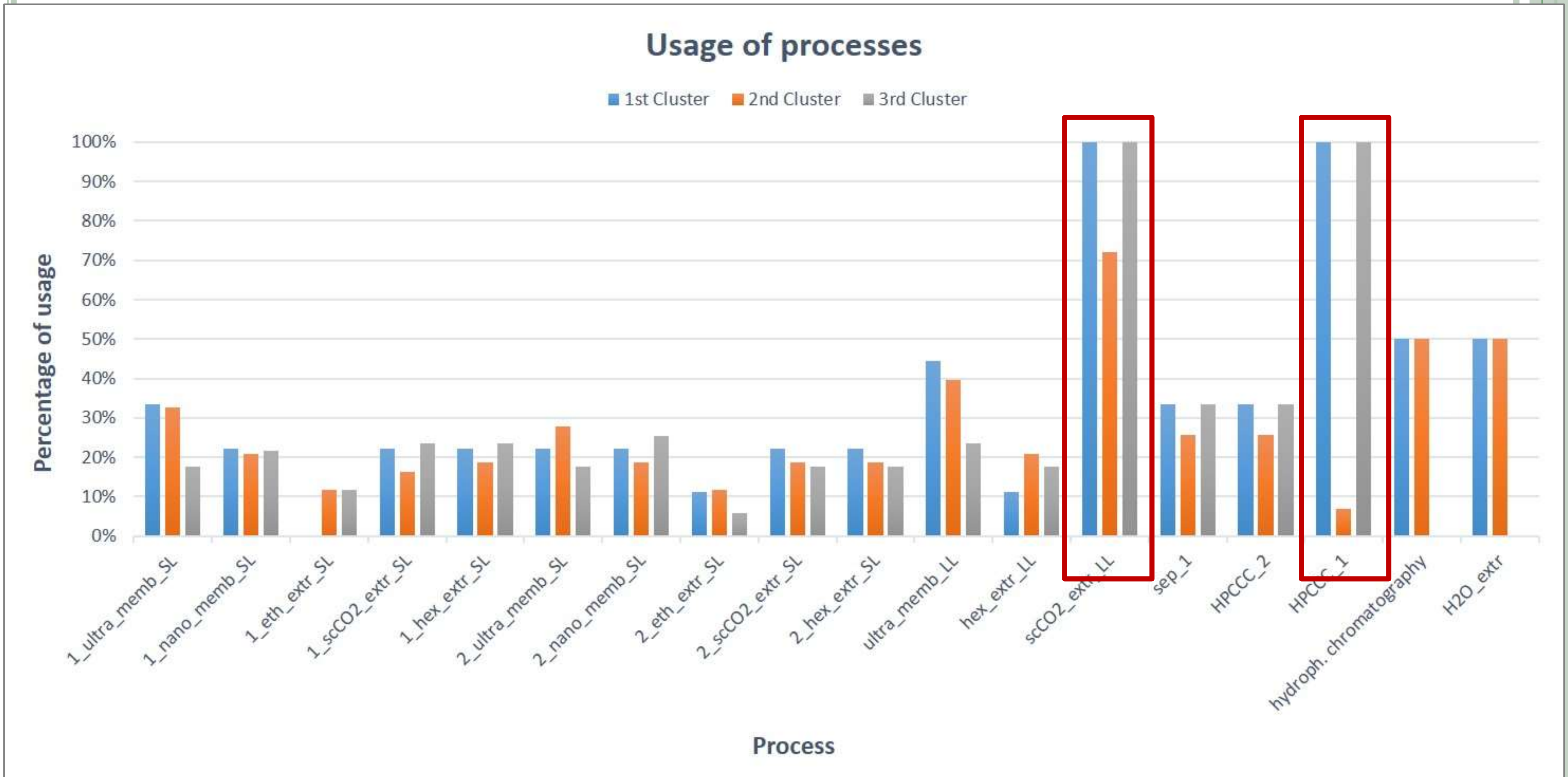
Plotting the ‘big picture’

<u>Multiple solutions</u>

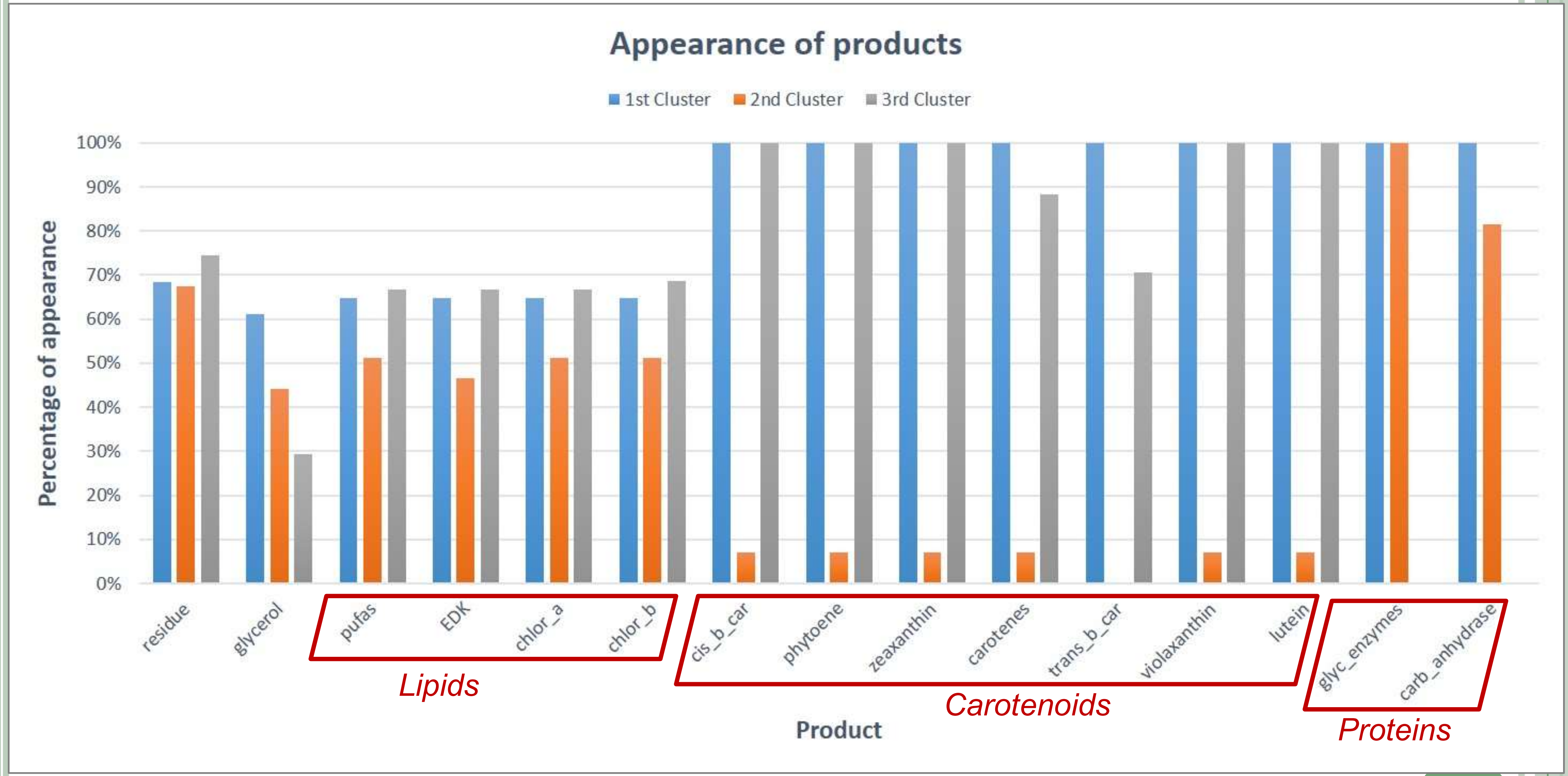
Study the impact of process/product selection on the profit



‘Popular technologies’



Popular products and product portfolios



Multi-algal plants and process flexibility

GENERALIZATION

1. Formulate value chains

Algae characteristics:

- Common properties
- High value chemicals as products

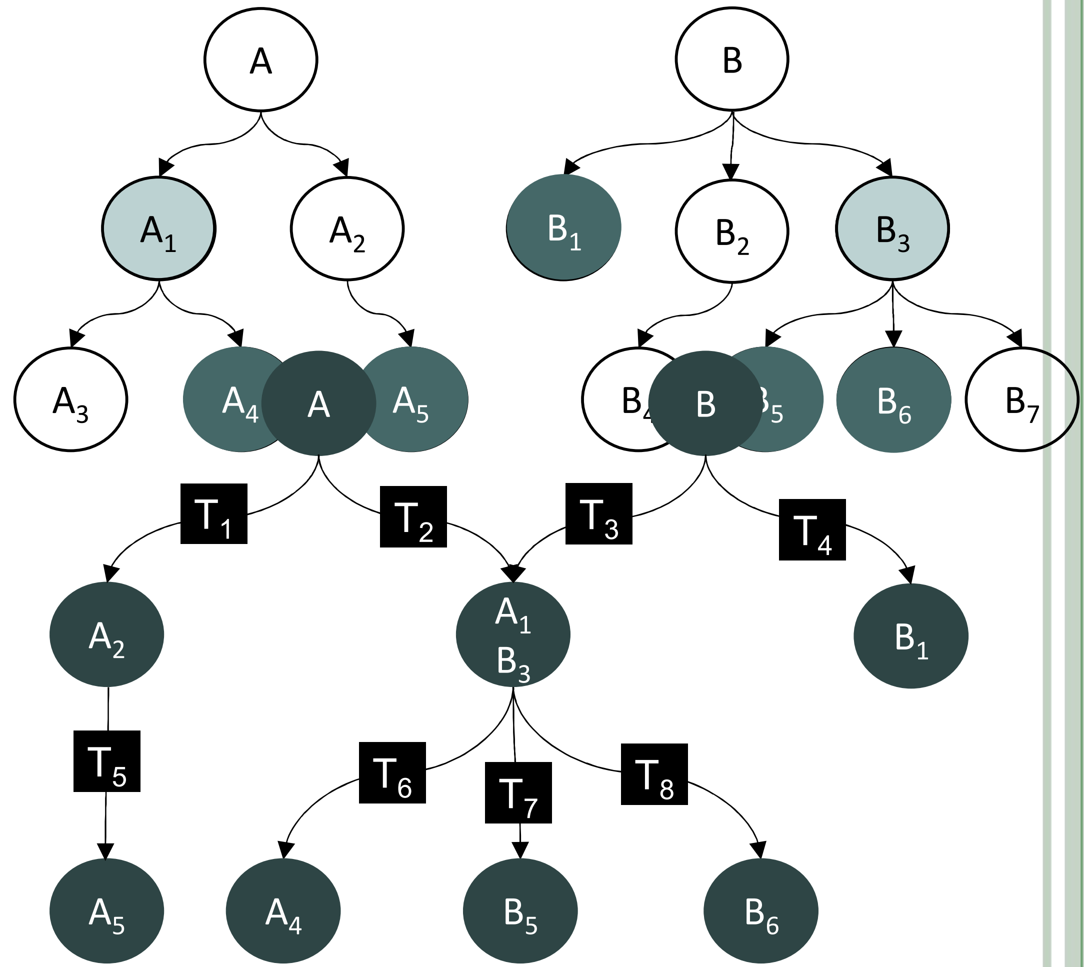
2. Identify common fractions

3. Customize product portfolios

Product selection:

- Market needs
- Price
- Amount
- Non competitive

4. Integrated value chain



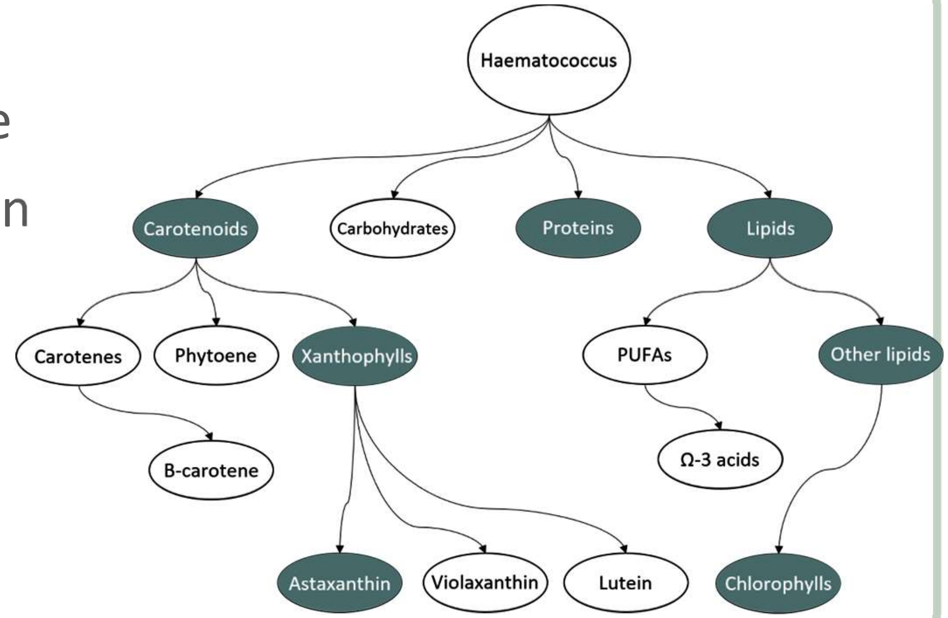
TARGETING FEEDSTOCK AND PRODUCTS

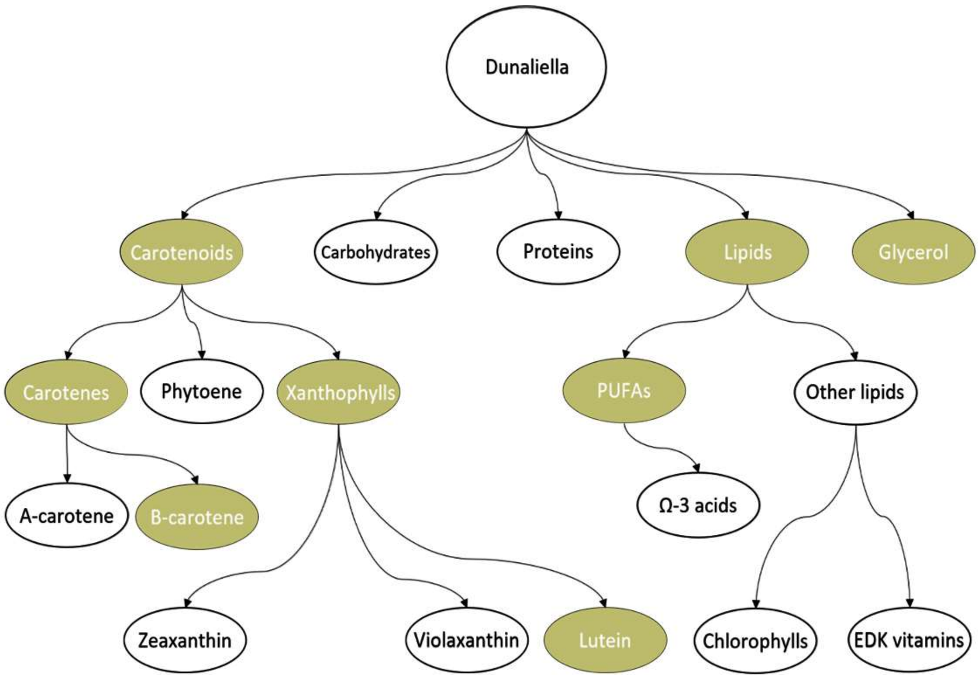
Microalgae feedstock

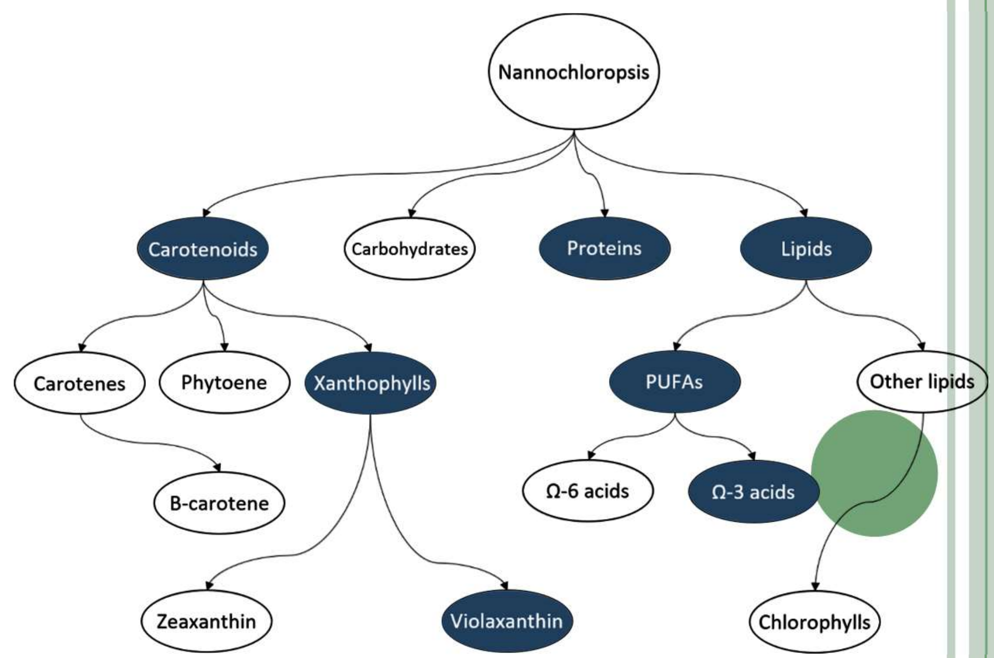
- Dunaliella
- Haematococcus
- Nannochloropsis

Target products

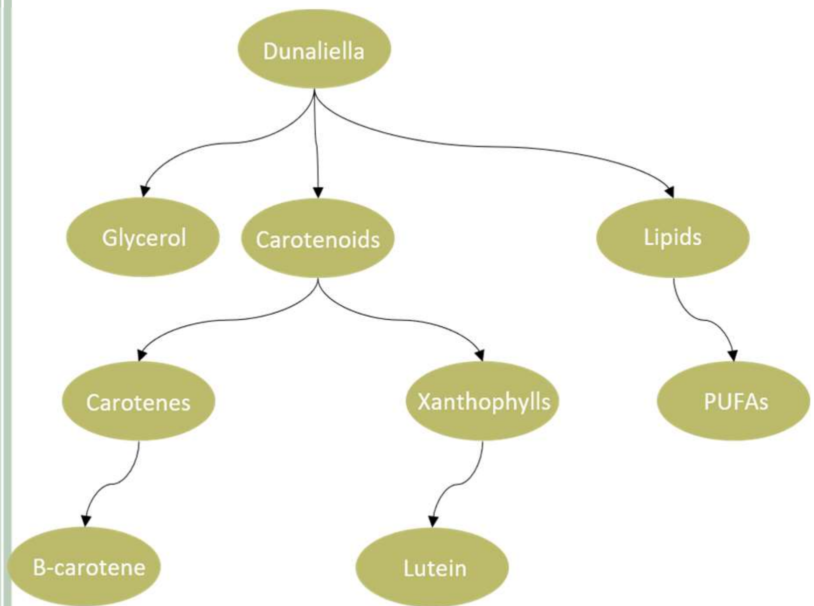
- B-carotene
- Astaxanthin
- Lipids



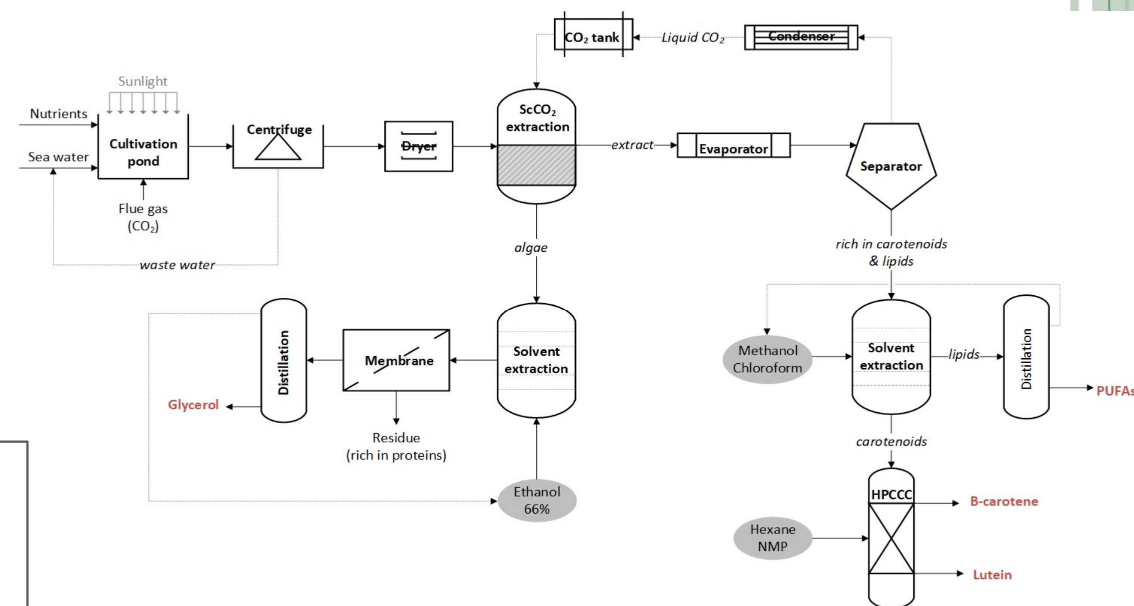


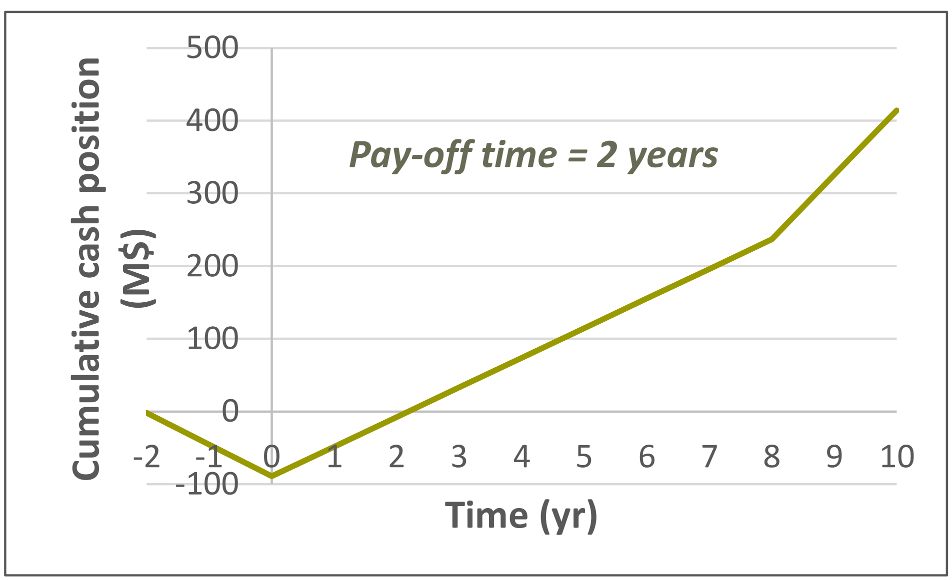


Single strain biorefinery - Dunaliella



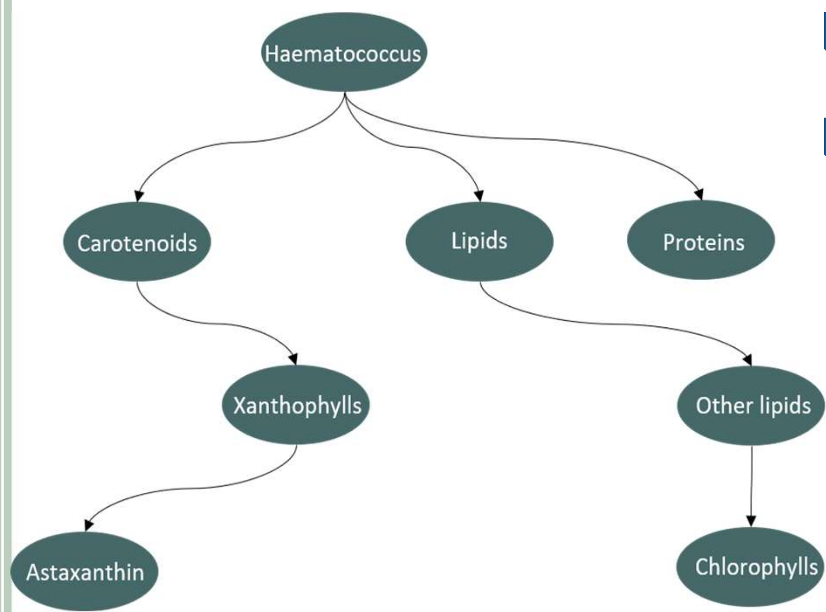
- Resistant to potential pollutants
- Growth in medium with high NaCl conc.



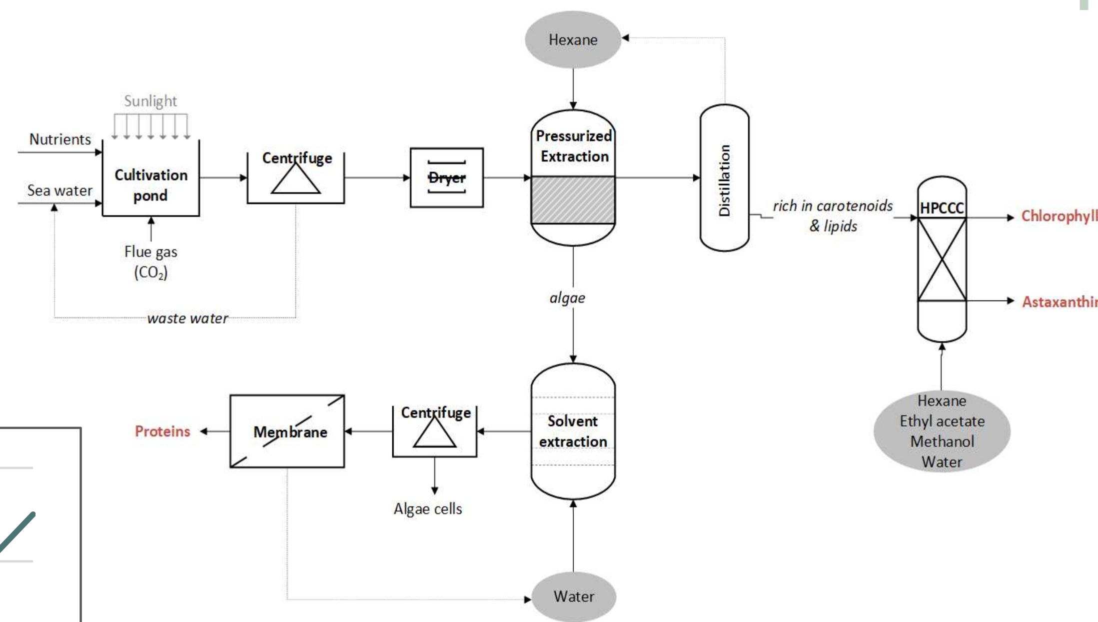


Capital cost (M$)	89
Operating cost (M$/yr)	31.2
Revenue (M$/yr)	126.6

Single strain biorefinery - Haematococcus

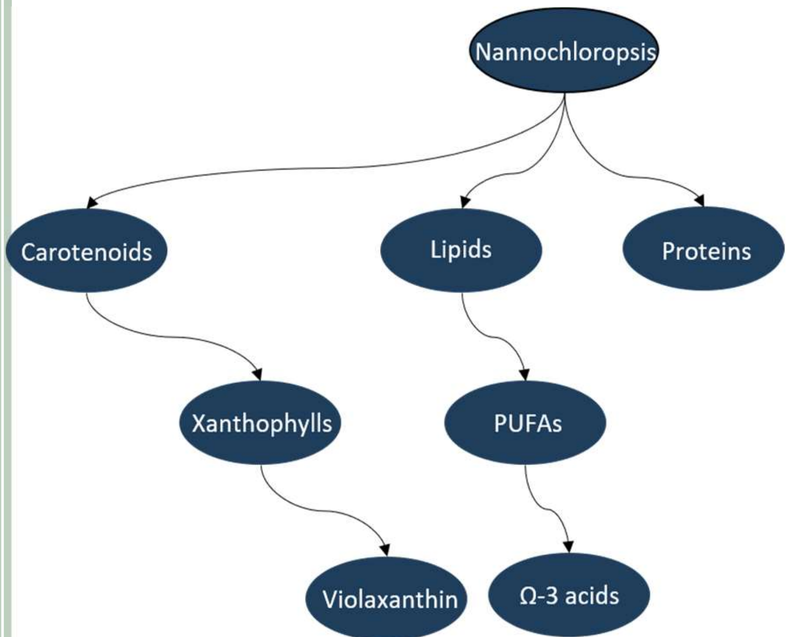


- Resistant species with thin cell wall
- Cells adaptable to external conditions by morphological adjustments

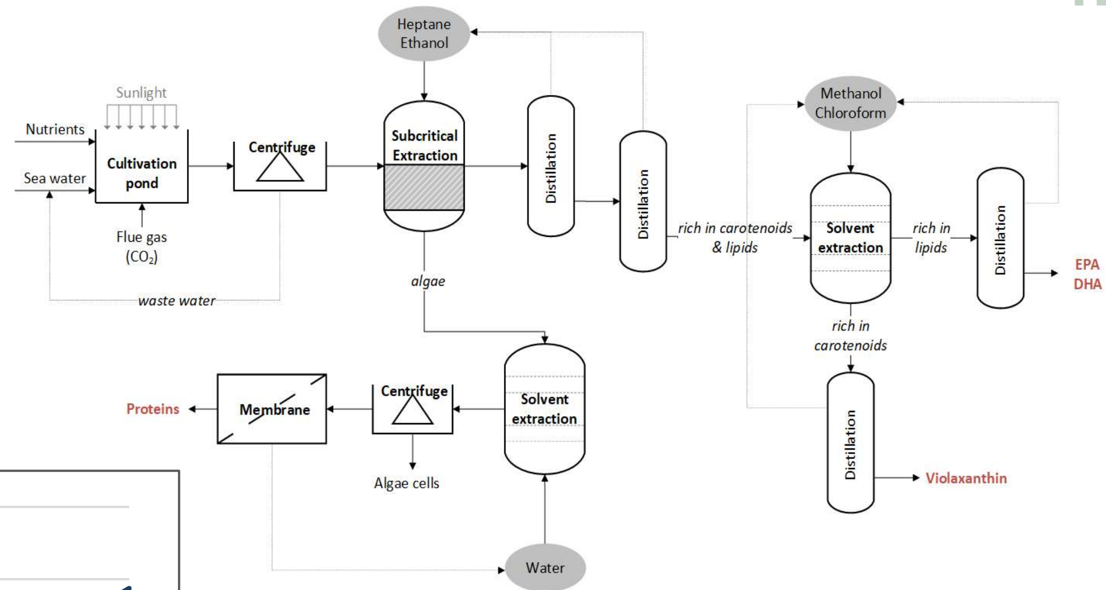


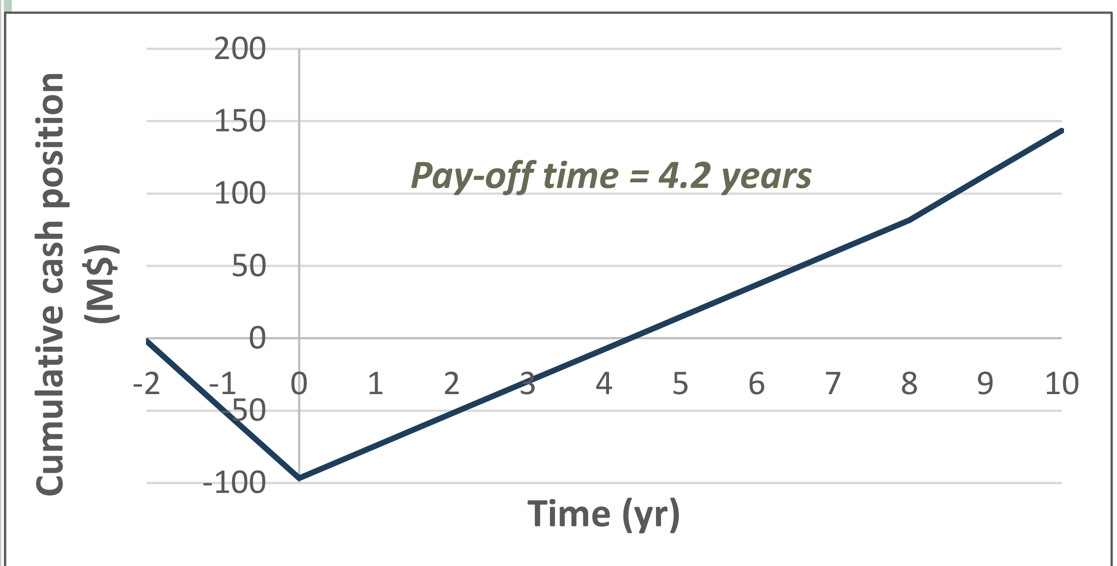
Capital cost (M$)	80
Operating cost (M$/yr)	25.7
Revenue (M$/yr)	108

SINGLE STRAIN BIOREFINERY - NANNOCHLOROPSIS



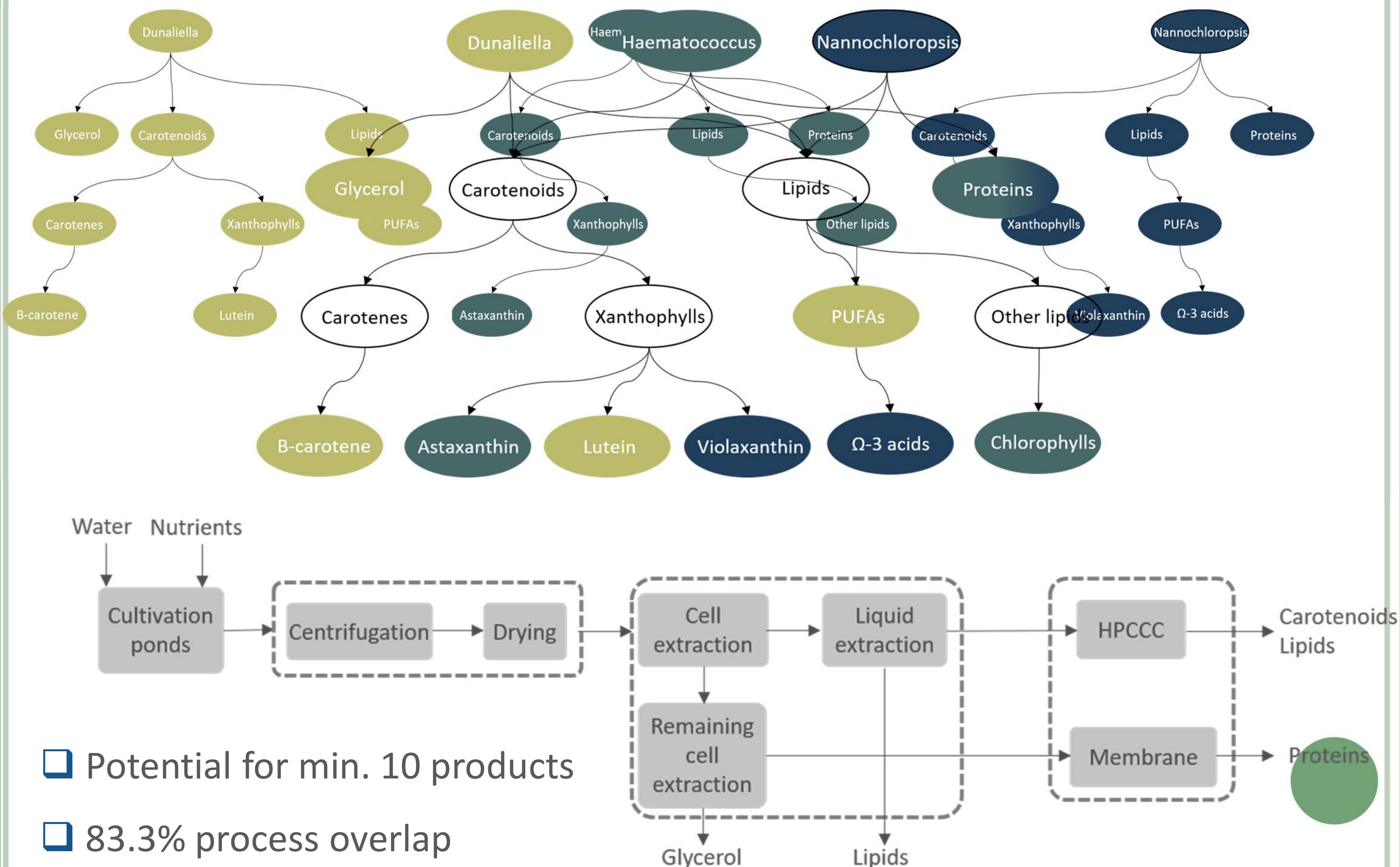
- Can store large amount of lipids
- Great candidate for outdoor mass cultivation





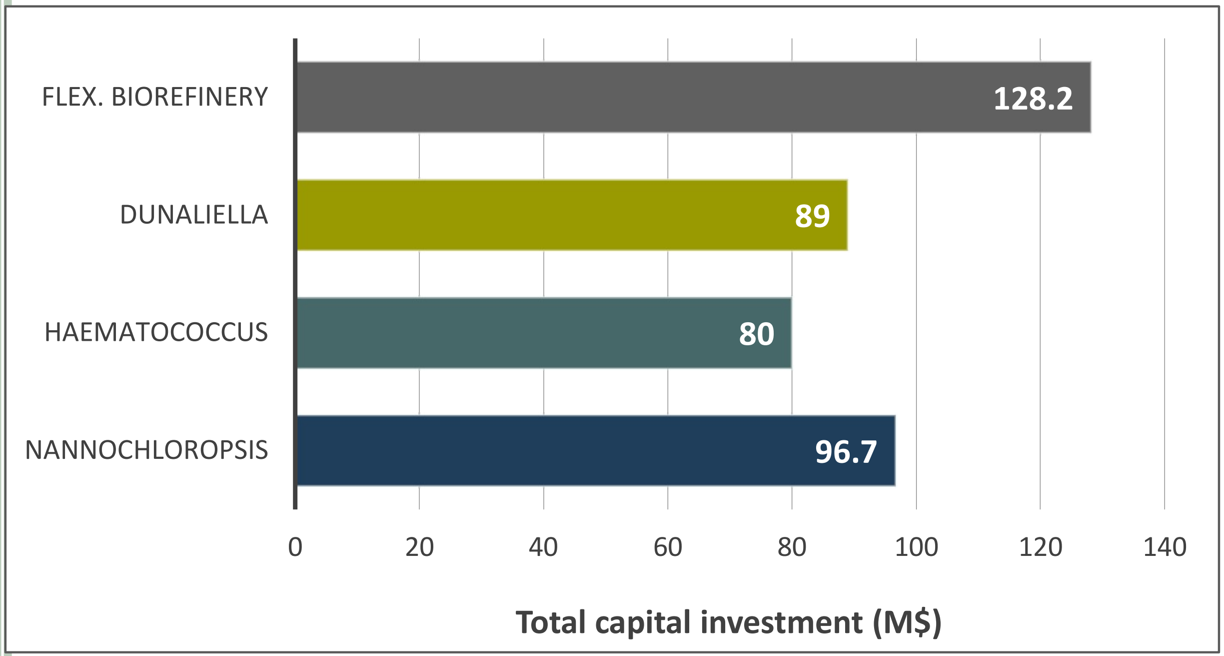
Capital cost (M$)	96.7
Operating cost (M$/yr)	35.1
Revenue (M$/yr)	44.2

BIOREFINERY MADE UP BY DIFFERENT STRAINS



- ❑ Potential for min. 10 products
- ❑ 83.3% process overlap

FLEXIBLE BIOREFINERY



Dunaliella 44%

Haematococcus 60%

Nannochlorospis 32,5%

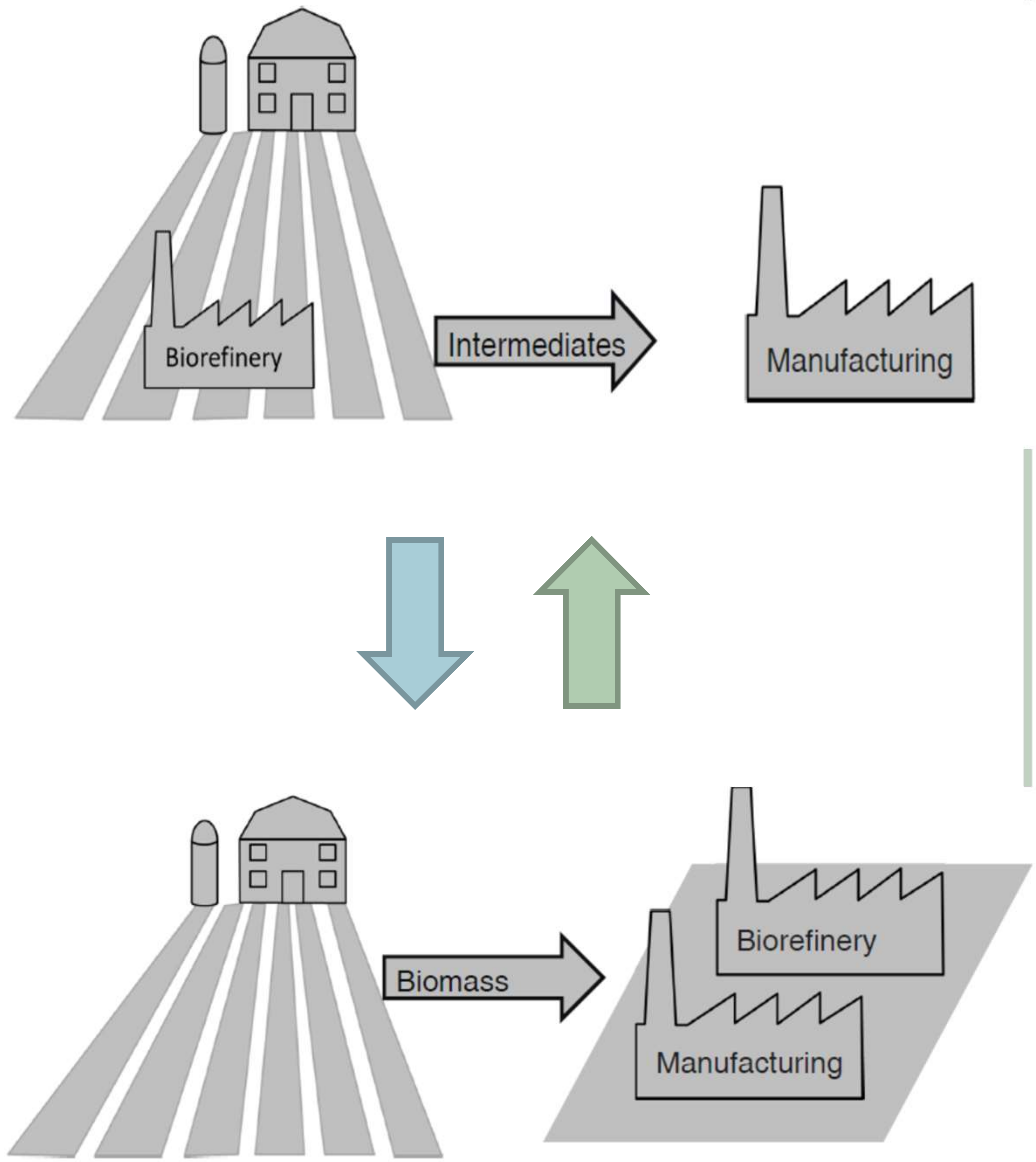
Flex. biorefinery

- Small increase in total investment enhances the biorefinery potential
- Requires extensive knowledge of microalgae value chains and candidate processes
- Coping with seasonality issues ➔ flexible biomass production
- Coping with volatile markets ➔ flexible product portfolio

STRENGTHENING SYMBIOSIS AND CIRCULAR ECONOMY TOWARDS INDUSTRIAL ECOLOGY: SOCIAL, URBAN AND MUNICIPAL FLOWS

BIOREFINERIES AND CO-LOCATION

- Integration of product manufacture is highly beneficial in terms of energy savings
  - 65-85% for increasing product portfolios
- Strong incentives for combining biomass fractionation with downstream conversion
- Reversing the picture should entail links with local communities



BUT WHAT IS THE POTENTIAL OF URBAN FLOWS?

Game-theoretical methods could shed light to a complex problem

Why game theory

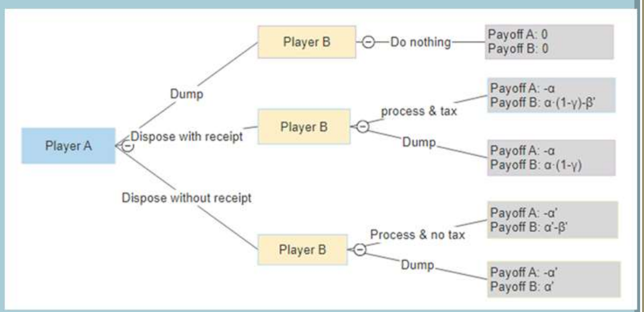
- Basis to research behavior and role of stakeholders
- Develop policy strategies to promote circular economy
- Win-win means that 'sum of profits' is not constant and pointing to (non-Pareto) non-zero-sum games
- Nash equilibria rather than Pareto optimal are correct objectives
- non-profit related criteria (e.g. threats, opportunities, stability, partner involvement, social benefits, etc.)

What in game theory

- Extensive forms (backward induction models: discrete decision, complete/incomplete information)
- Bilevel optimization: along the lines of Stackelberg analysis
- Mixed-strategy Nash equilibria
- Epistemic game theory and pre-occupations on stakeholders

GAME THEORY - INDICATIVE APPLICATIONS

MSW management: backward induction, complete information



No-Subsidies

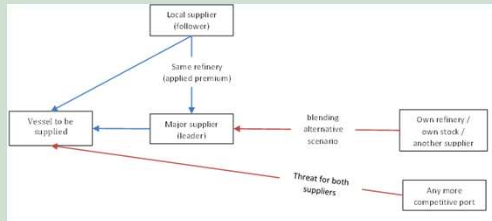
		Player B	
		B.1	B.2
Player A	A.1	0, 0	0, 0
	A.2	$-\alpha$, $\alpha\cdot(1-\gamma)-\beta'$	$-\alpha$, $\alpha\cdot(1-\gamma)$
	A.3	$-\alpha'$, $\alpha'-\beta'$	$-\alpha'$, α'

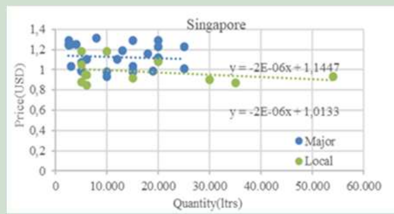
Subsidies

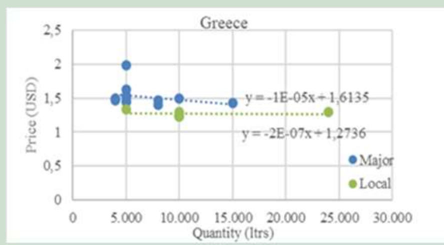
		Player B	
		B.1	B.2
Player A	A.1	0, 0	0, 0
	A.2	$-\alpha+x_1$, $\alpha\cdot(1-\gamma)-\beta'+x_2$	$-\alpha+x_1$, $\alpha\cdot(1-\gamma)$
	A.3	$-\alpha'$, $\alpha'-\beta'$	$-\alpha'$, α'

- Lawbreaking is consistently encouraged
- Subsidies are unhelpful
- Circular economy could turn stability tables to lawful markets

Marine lubricant markets: Bilevel optimization

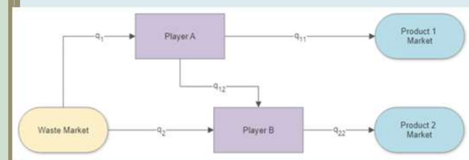


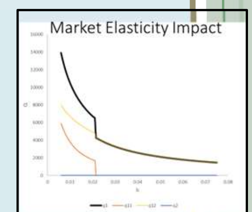




- Confirmed existing market share
- Premium as major threat
- Weak position of local producers

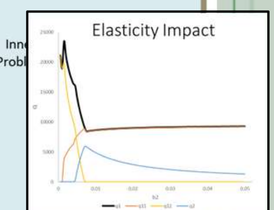
Circular economy markets: Bilevel optimization

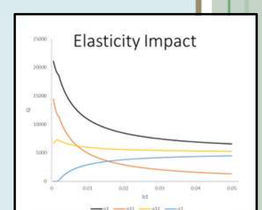




Outer Problem

Maximize p1	Target Maximization
Subject to	
Maximize p2	P2 Profit Maximization
Subject to	
$p_2 = a_2 - b_2 \cdot q_{22}$	Market 2
$P_2 = p \cdot q_2 + p_2 \cdot q_{22} + p' \cdot q_{12} - C_2$	P2 Profit
$C_2 = c_2 \cdot q_{22}$	P2 total cost
$p_1 = \alpha_1 - b_1 \cdot q_{11}$	Market 1
$P_1 = p \cdot q_1 + p_1 \cdot q_{11} - C_1$	P1 Profit
$C_1 = c_1 \cdot q_{11} + p' \cdot q_{12}$	P1 total cost

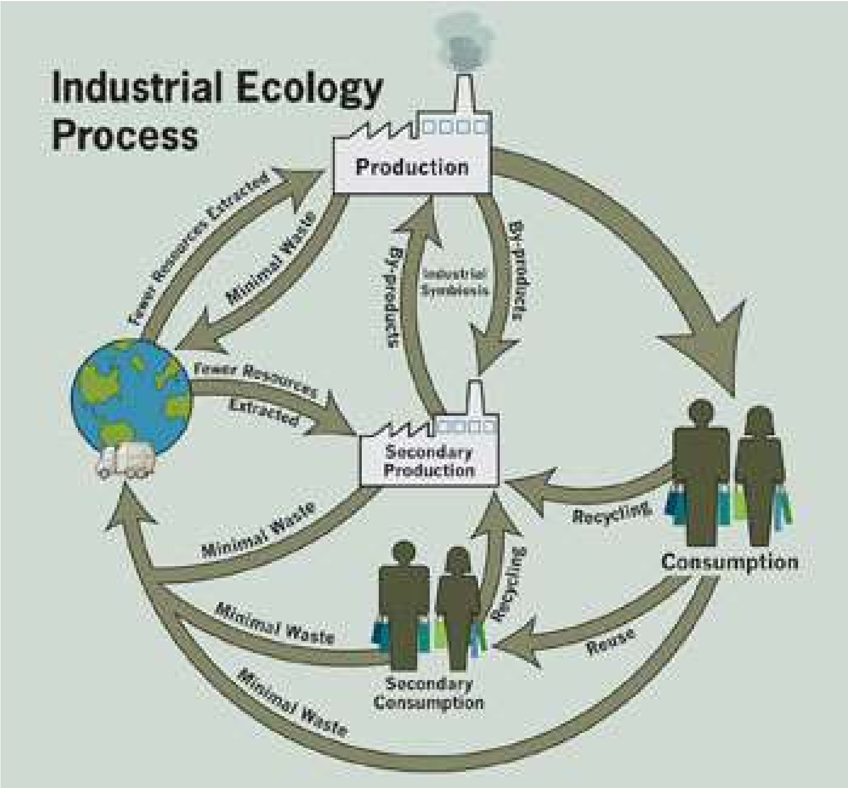




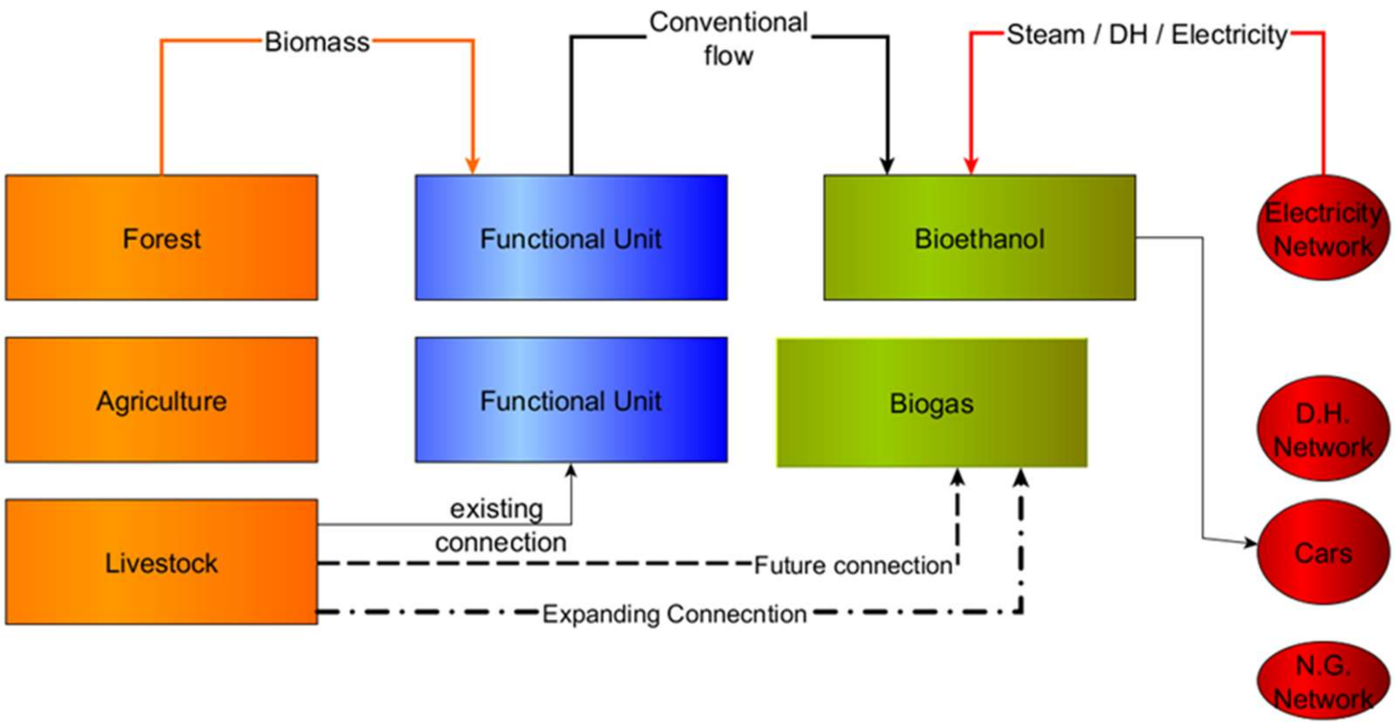
- Significant differences with conventional markets
- Conventional Stackelberg does not apply in a usual form

INDUSTRIAL SYMBIOSIS: A PRACTICE OF NETWORKING

- The use of waste streams as resources to other industries (materials, energy)
- Essential part of Industrial Ecology
  - Closed life cycles
    - Material flows
    - Energy flows
- Differences from recycling
- Often preferred over recycling
  - Long recycle paths
  - Expensive footprints

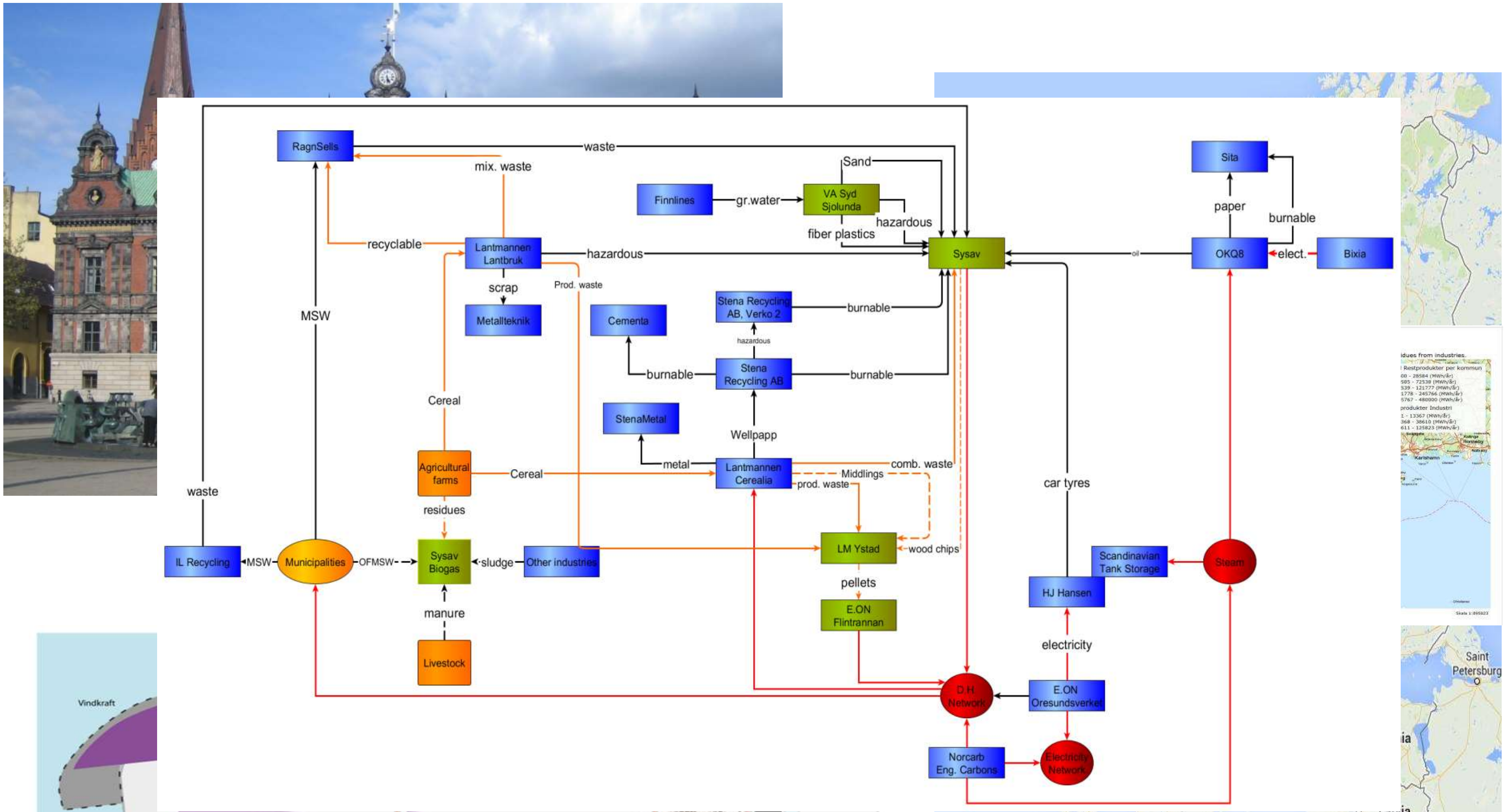


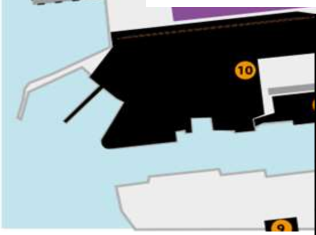
MODELLING INDUSTRIAL PORTS



- Biomass supplies (orange), industrial units (blue), bioenergy producers (green), energy consumers (red)
- Each FU features mass and energy balances
- Matching technology has been used to analyze and assess links and possible networks

MALMOE

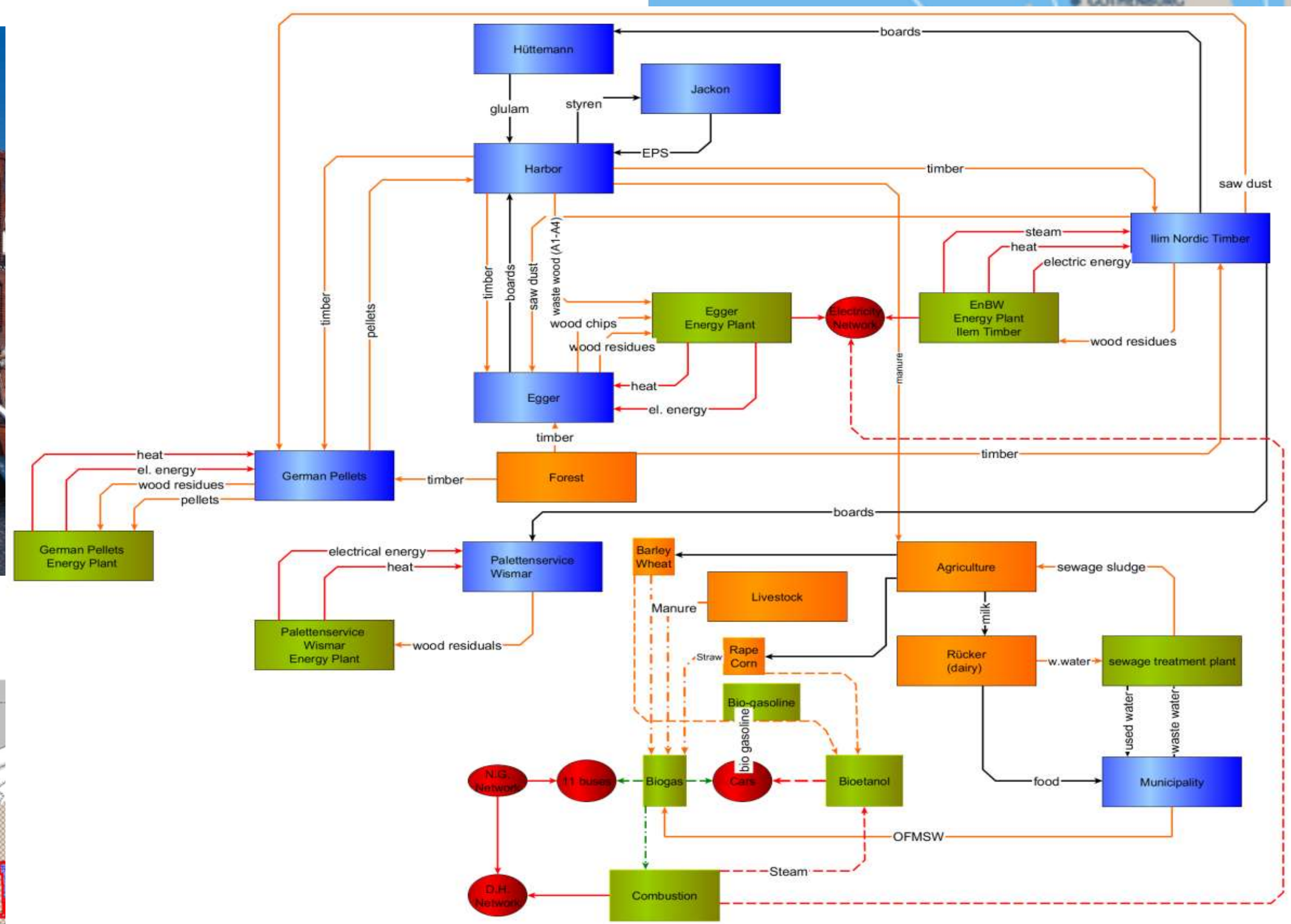




Bioenergy potential	38,3 MW Internal (direct combustion and biogas)	149 MW external (direct combustion and biogas)
Functional Units	16 existing within the port area	2 new
Connections	42 existing	5 new

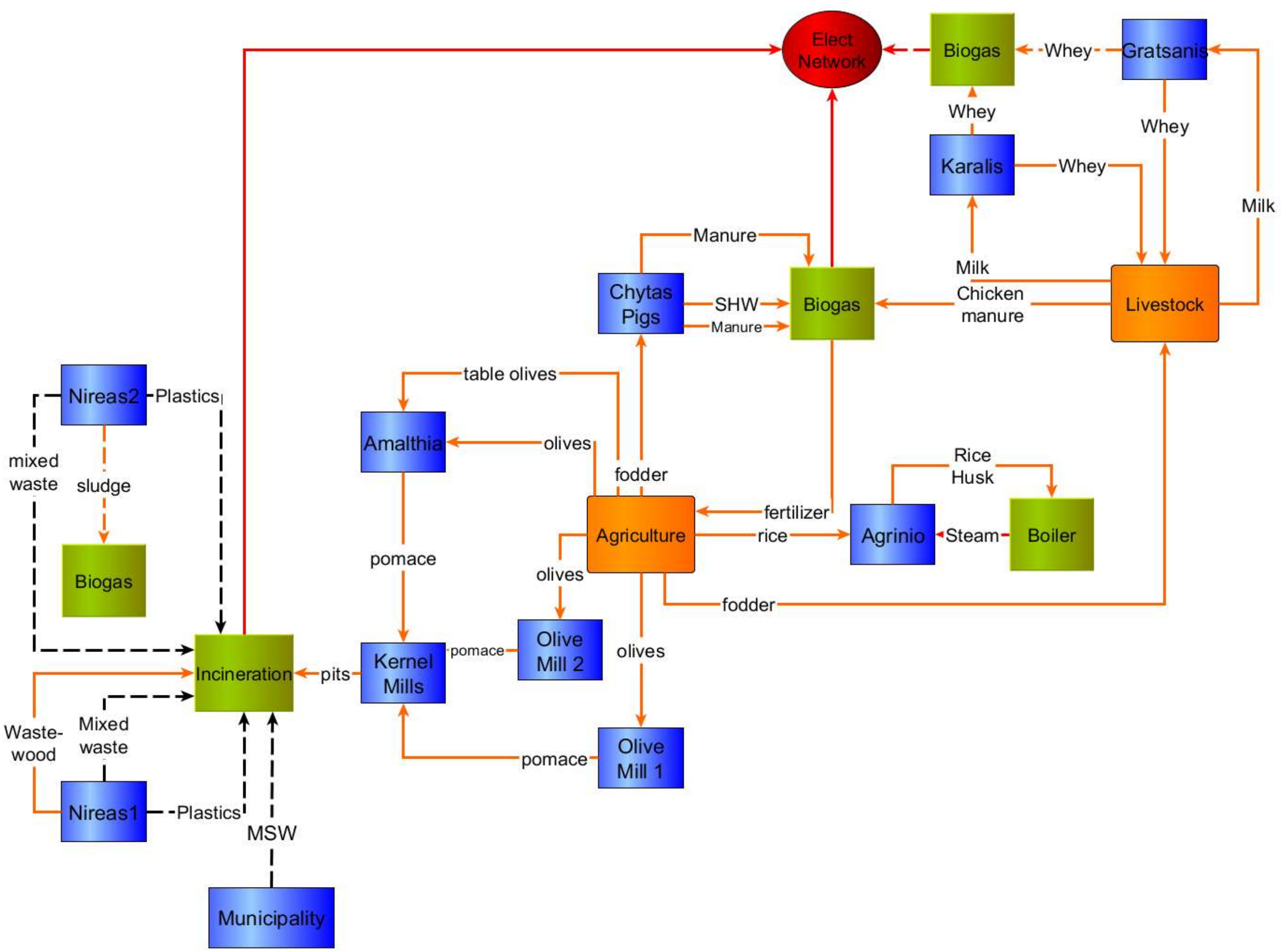
e·on

Wismar



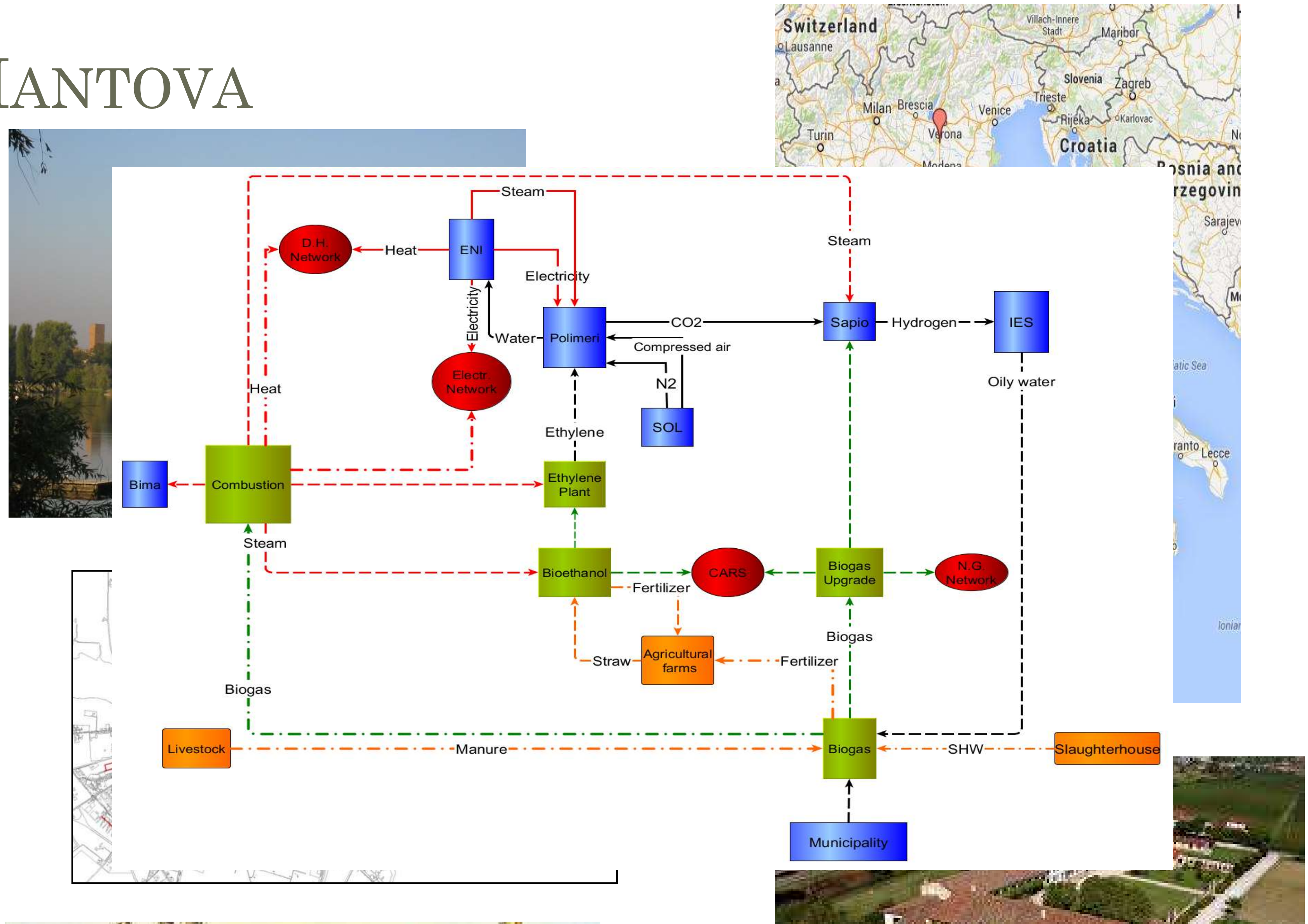
Bioenergy potential	69MW bioethanol or 129MW direct combustion	16MW biogas
Functional Units	10 existing industries	3 new
Connections	42 existing	12 new

Astakos



Bioenergy potential	137MW (direct combustion)	20MW biogas based on manure
Functional Units	9 industries were interviewed which belong to the greater area of Astakos	3 new
Connections	25 existing connections	5 new connections

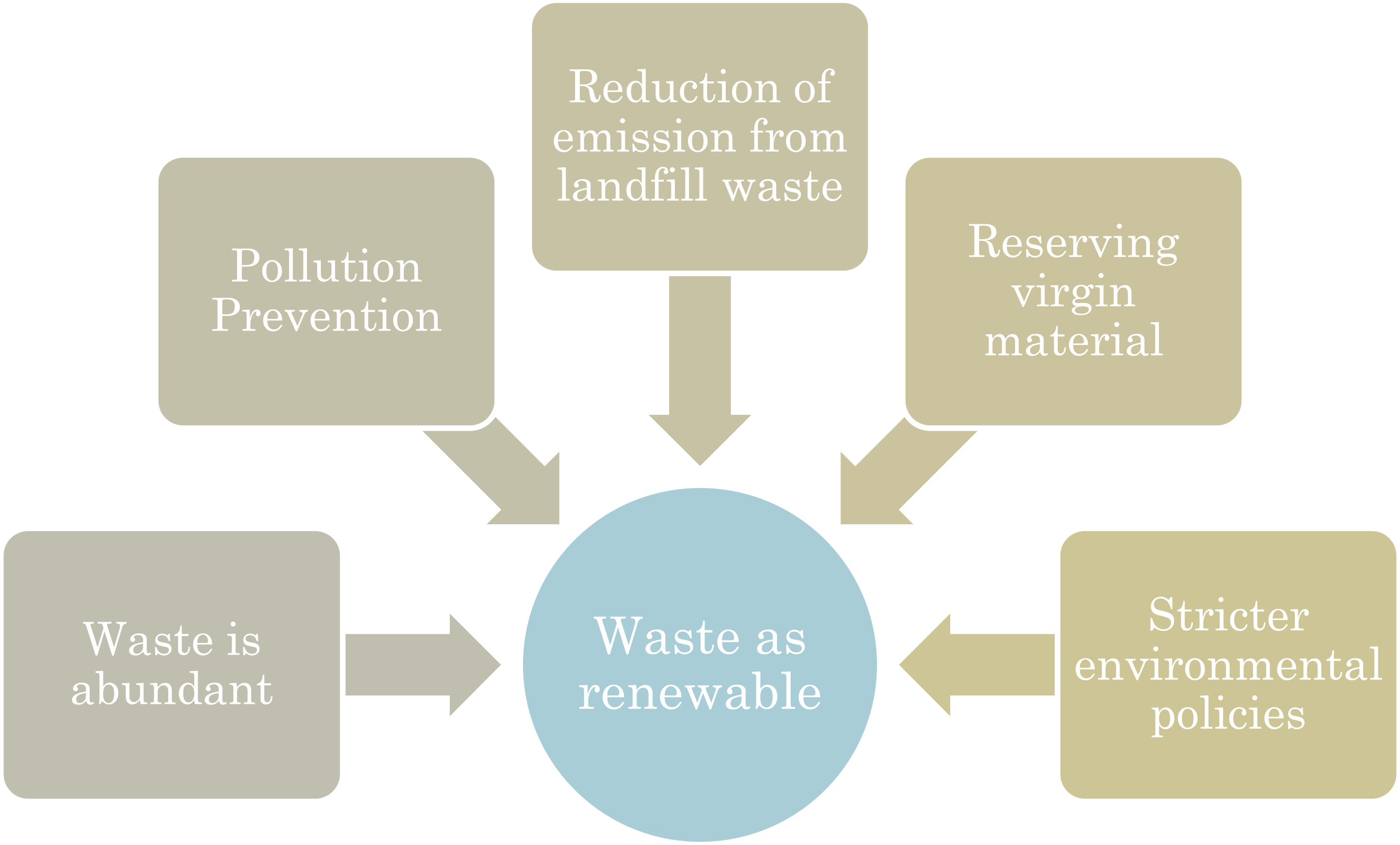
MANTOVA



Bioenergy potential	681 MW (411MW biogas and 270MW ethanol)	
Functional Units	5 existing industries	4 new Functional Units
Connections	8 existing	21 new

WASTE AS A RESOURCE: INDUSTRIAL SYMBIOSIS AND CIRCULAR ECONOMY

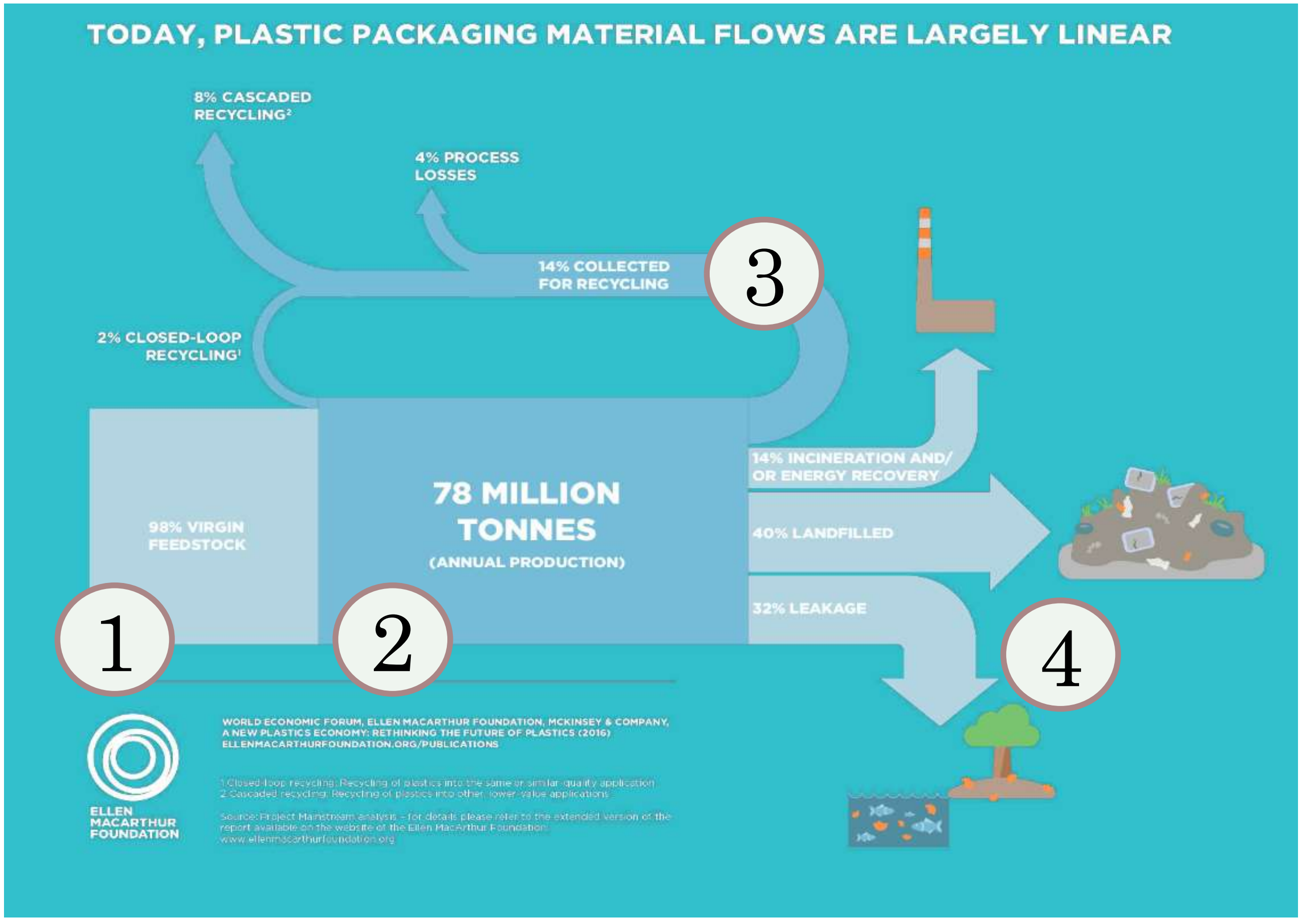
WASTE AS RENEWABLE

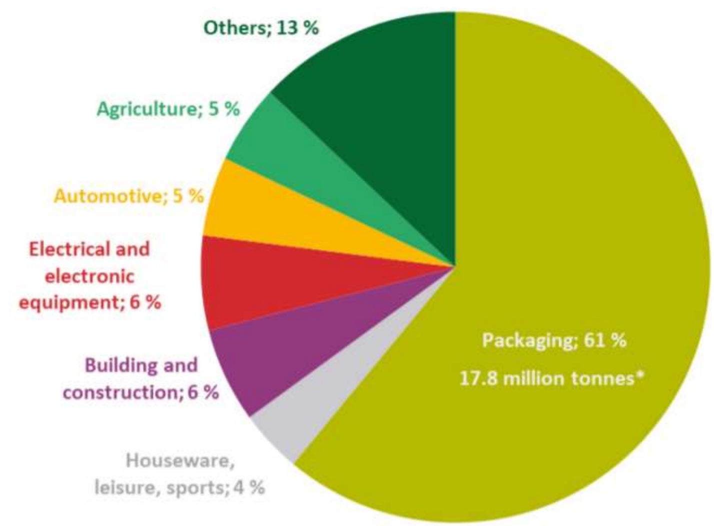


- Europe already treats 50 million ton of wastes at WTE plants – generating electricity for 27 million people

Confederation of European Waste-to-Energy Plants (CEWEP)

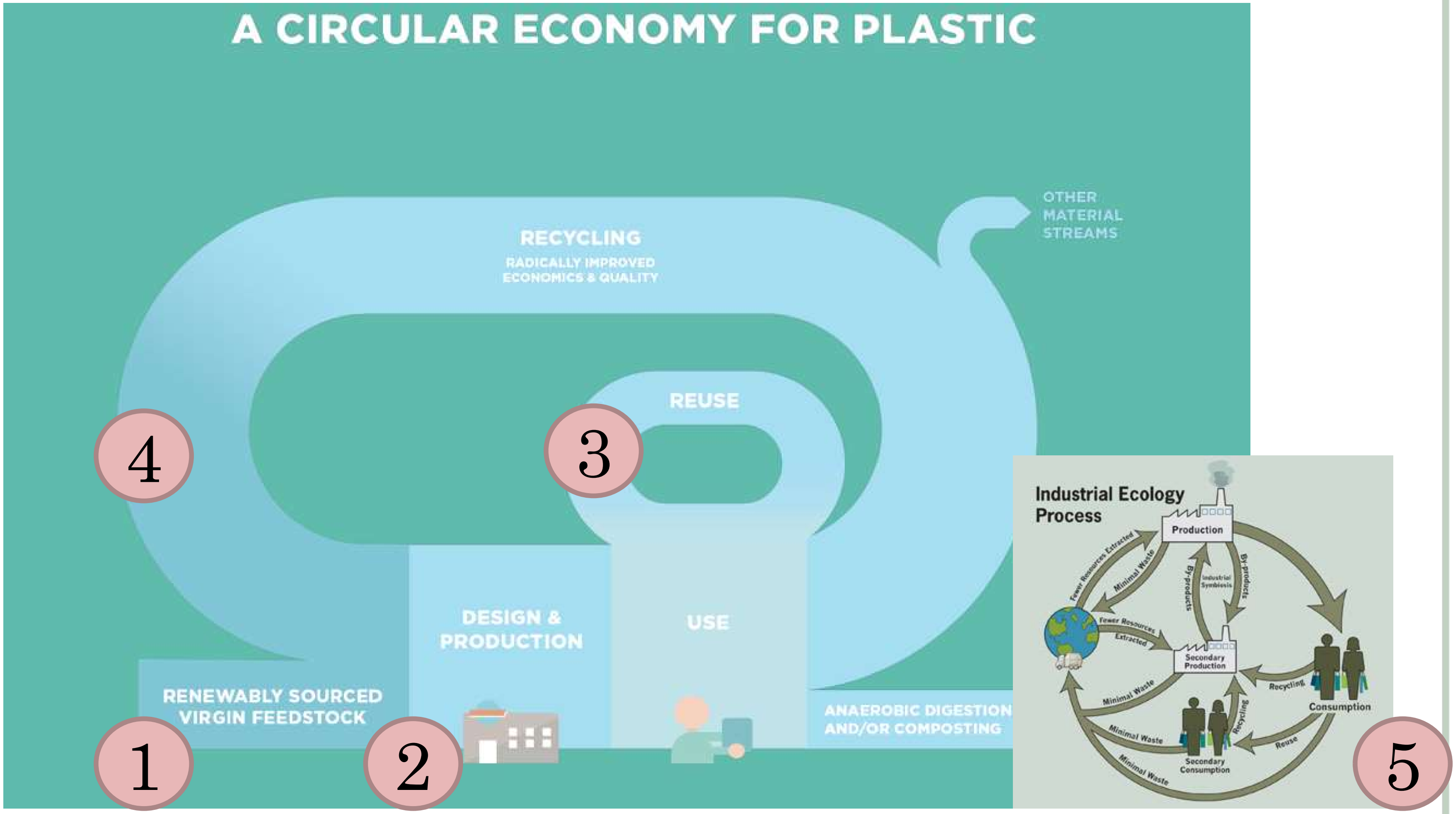
THE OVERALL BALANCE OF PLASTICS TODAY





- Entire production depends on finite, virgin resources (1)
- Poor technology (2) and business models (3) for recycle and re-use
- Plastics discarded either as waste or in waste to energy projects (4)

TOWARDS A SUSTAINABLE CIRCULAR MODEL



- New feedstocks: renewables and re-used plastics
- Production to enhance re-use and lifetime in internal cycles
- Sustainable recycling in the context of circular economy and industrial symbiosis

THE LARGEST WASTE STREAMS

Construction & Demolition Waste

750 millions tons
(Europe)

Textile Waste

0.1 billions tons
(globally)

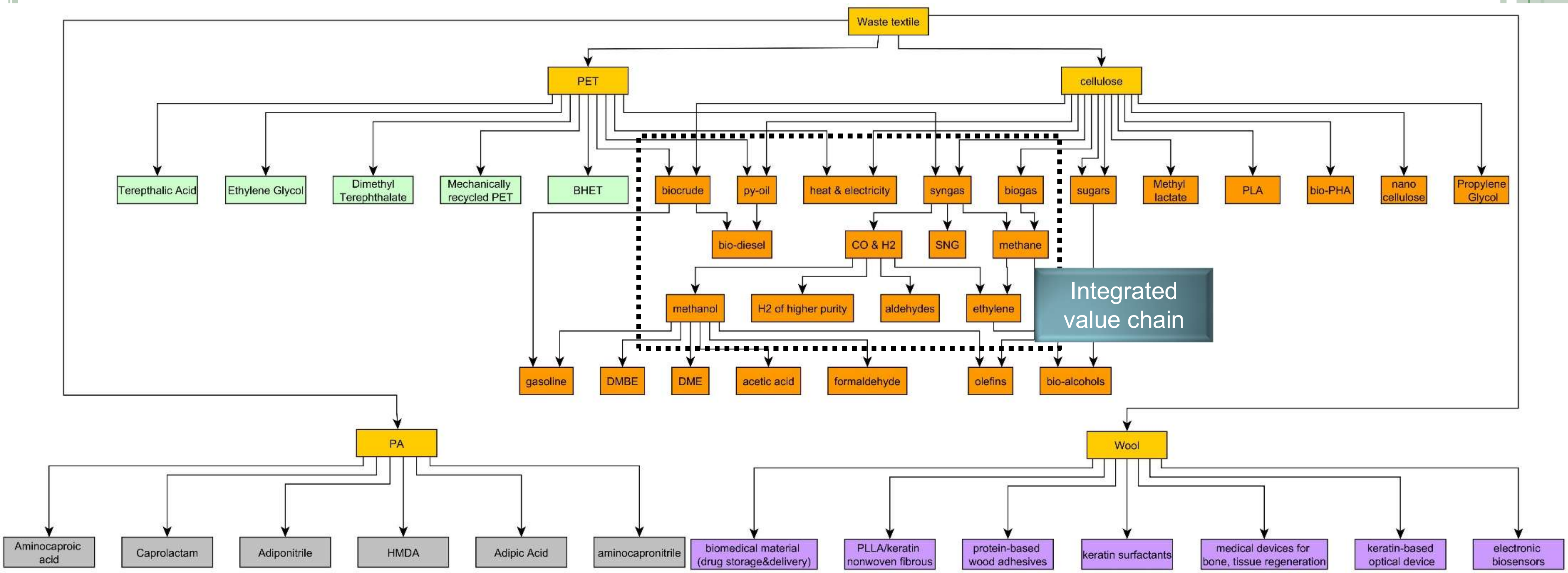
Food Waste

1.6 billions tons
(globally)

Municipal Solid Waste

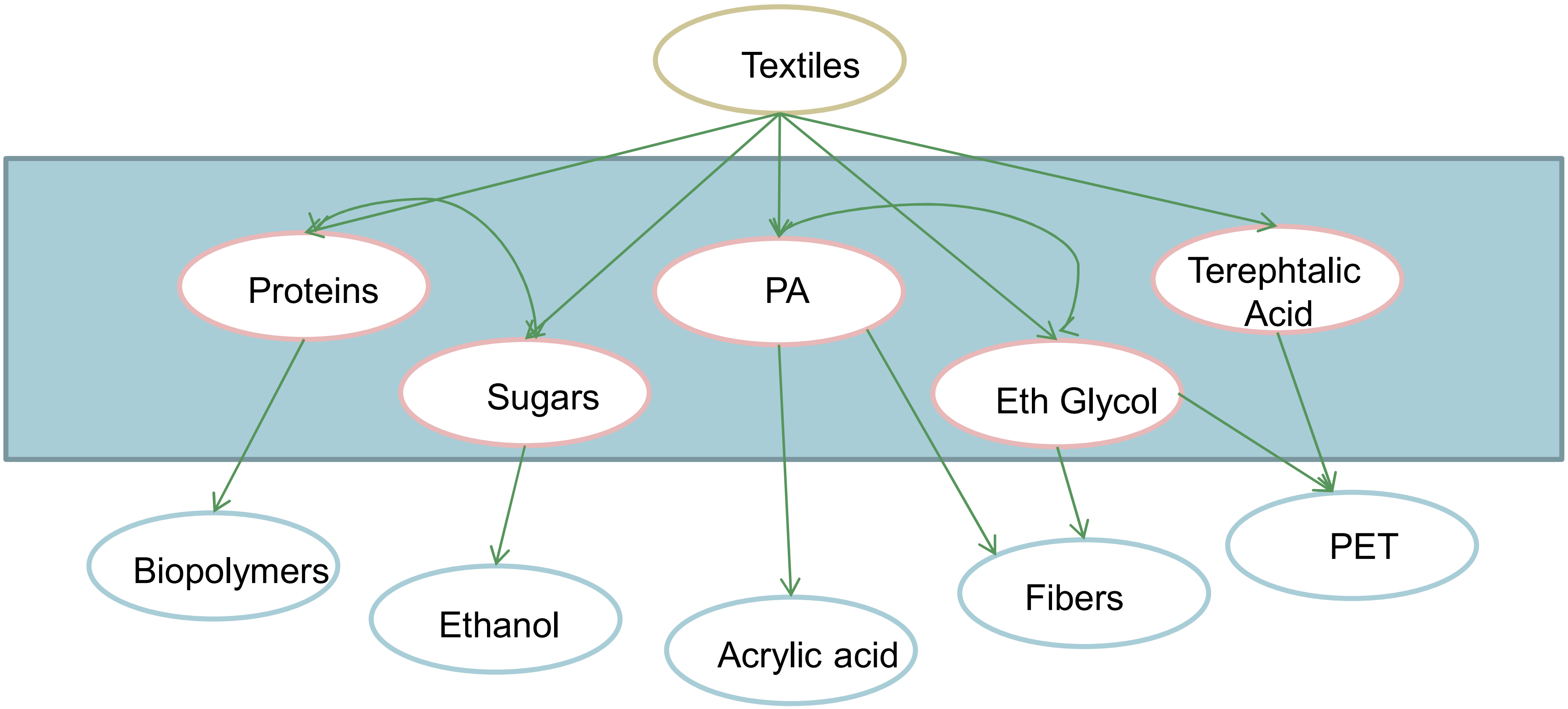
2.12 billions tons
(globally)

THE TEXTILE VALUE CHAIN



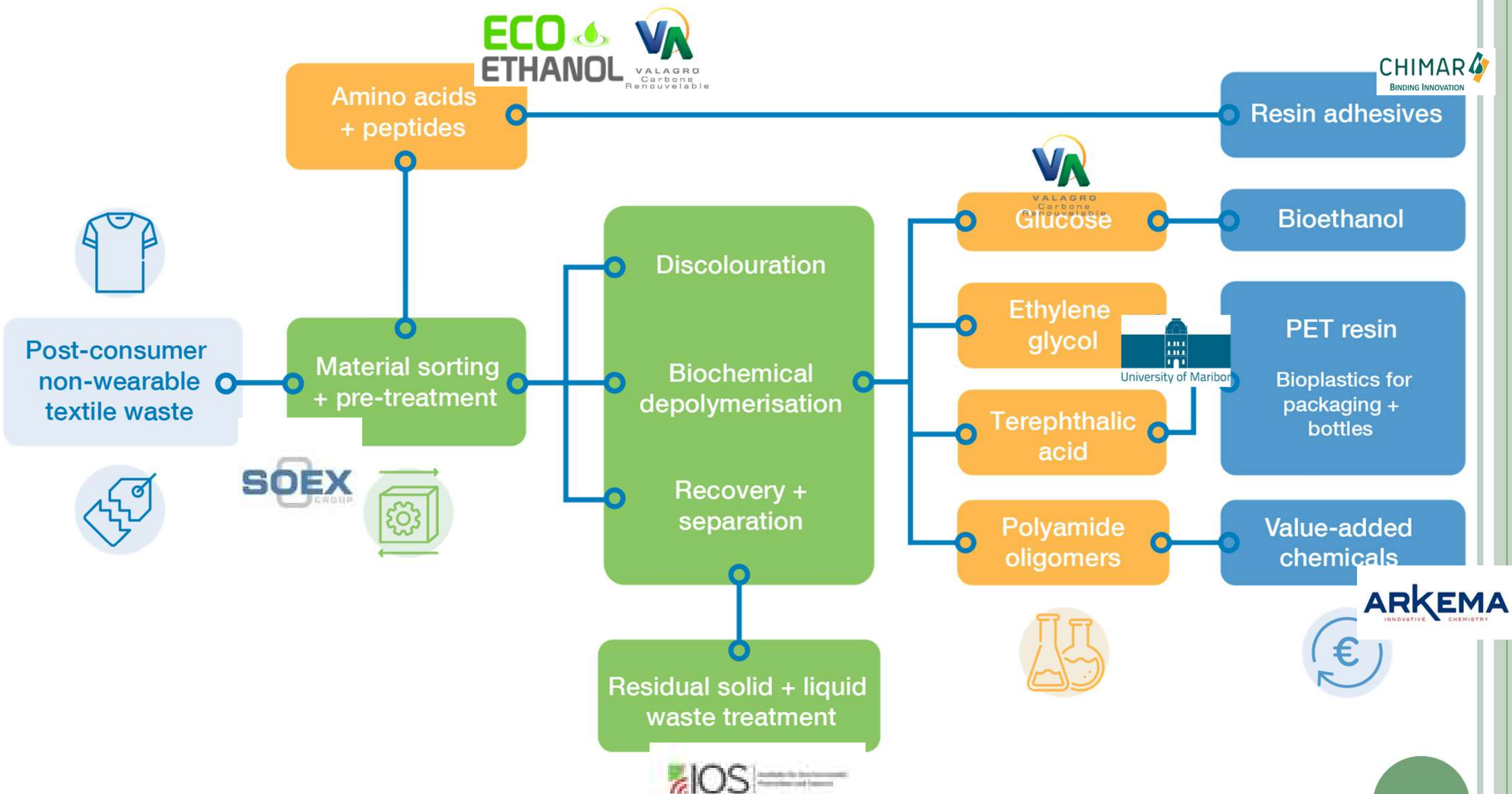
DRIVING A CIRCULAR ECONOMY PARADIGM ON TEXTILES

- More than 300,000 tons/year only available in France



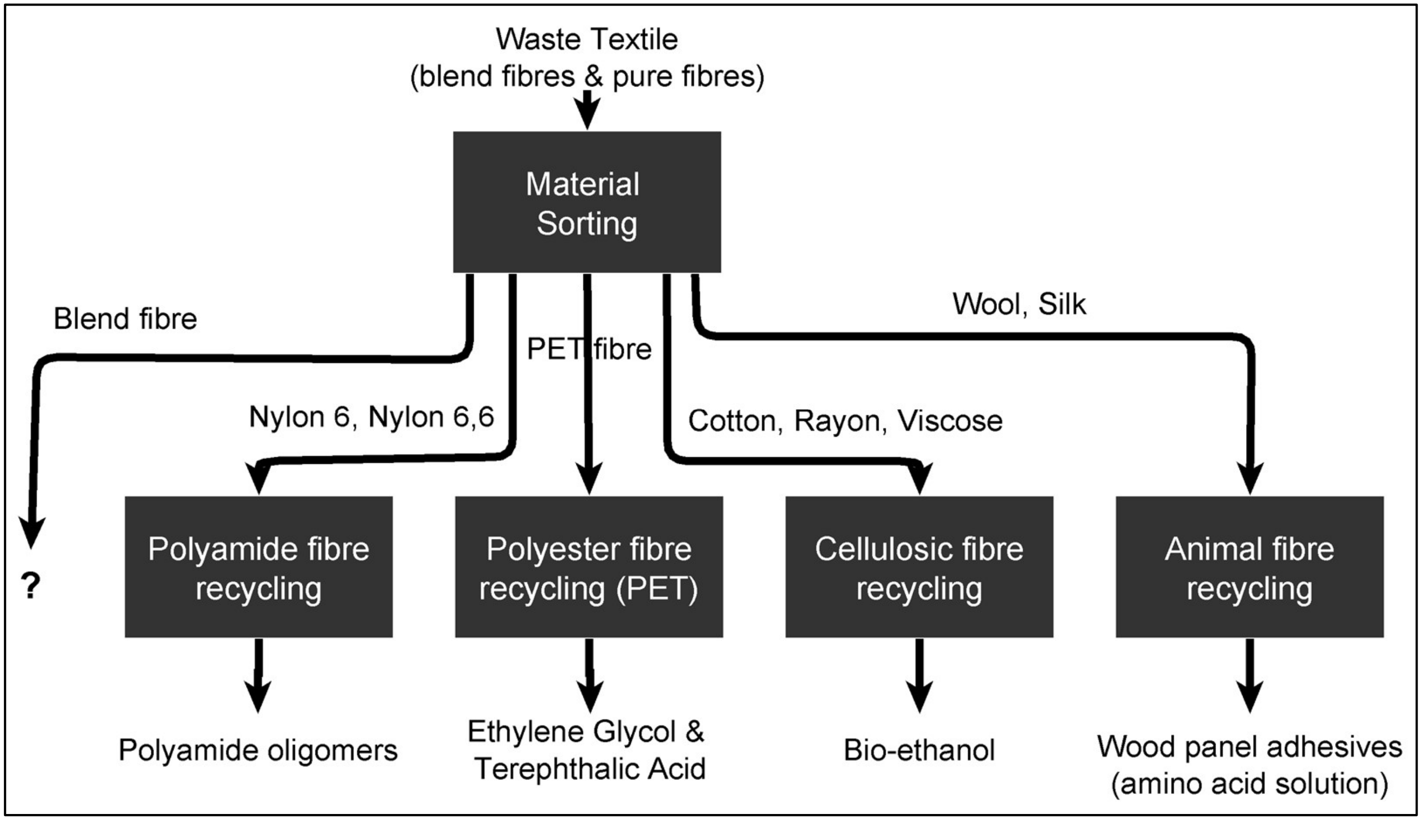
- Build scale with further integration: other biorefineries **(industrial symbiosis)** & urban flows

The RESYNTEX project



Much more than any other projects, the systems approach has been critical to drive iterations, amendments and modifications…

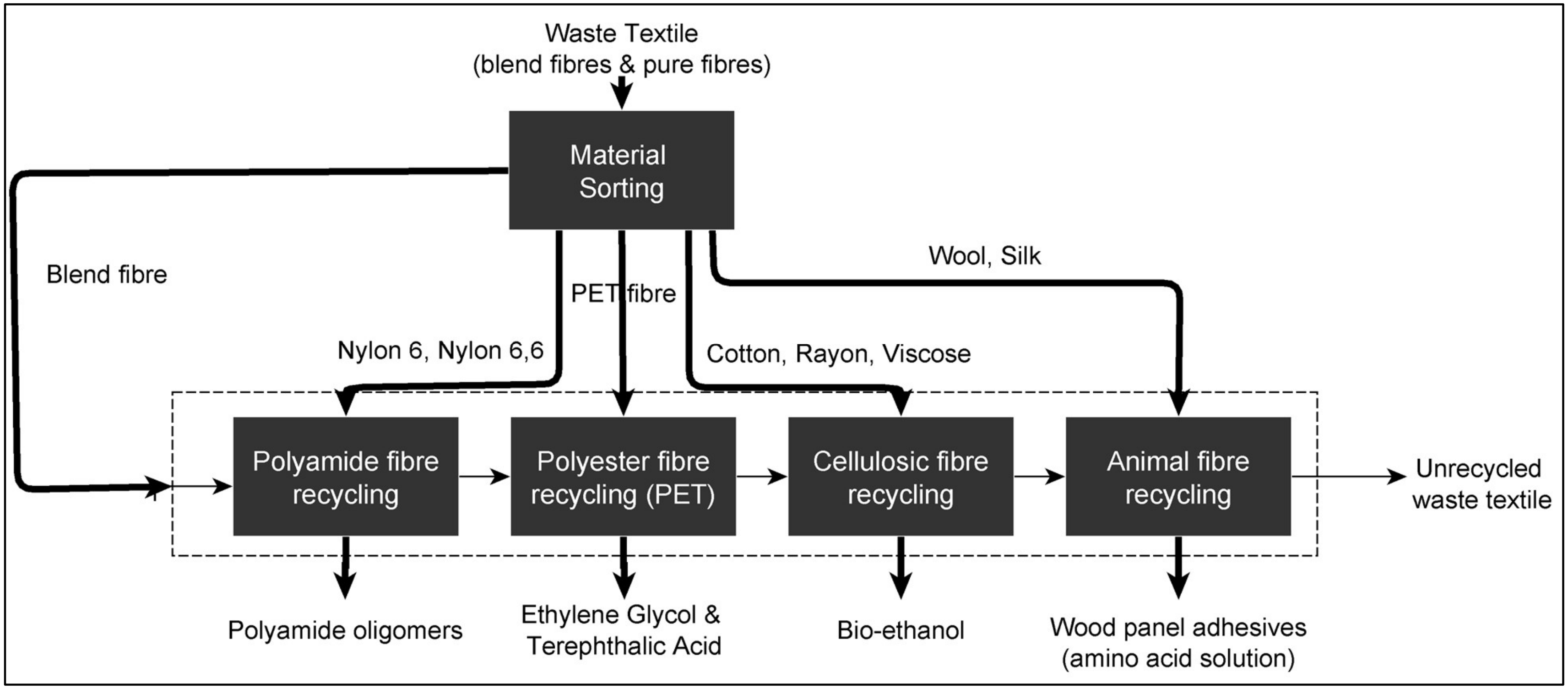
PHASE 1: DISCRETE PROCESSING



Challenge | 50% of waste textile is blend fibres

Motivation | Integrated waste textile blends in process design

Phase 2: Cascade-discrete processing



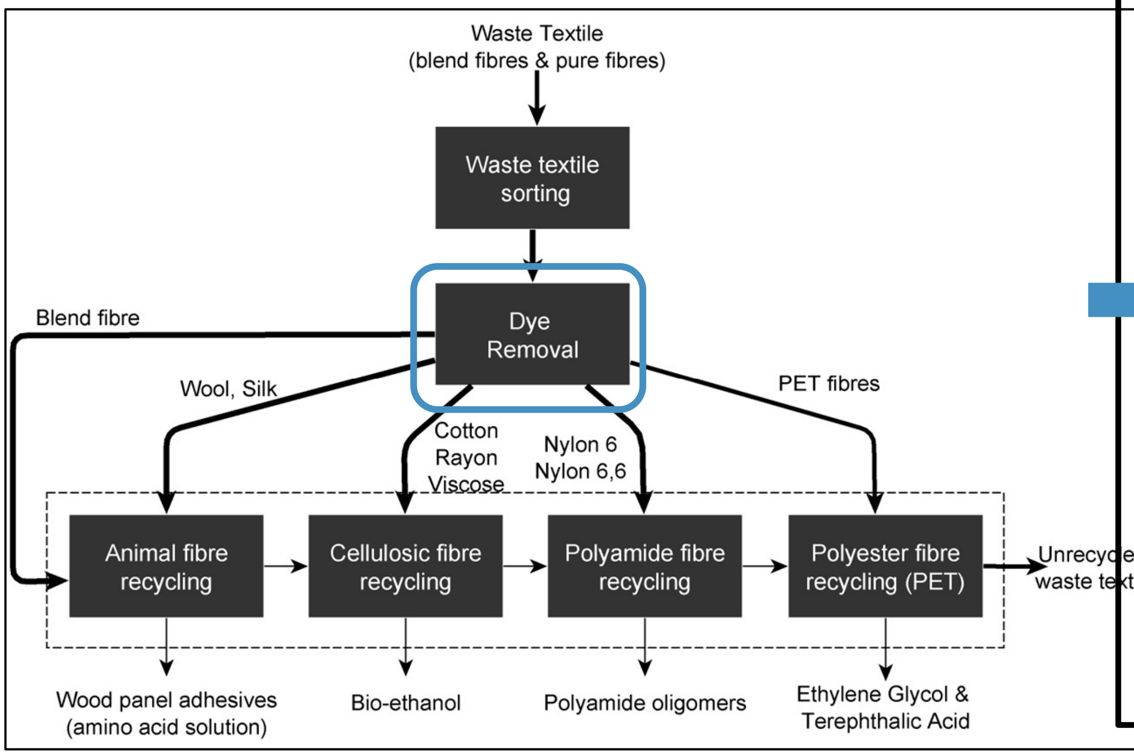
Challenge

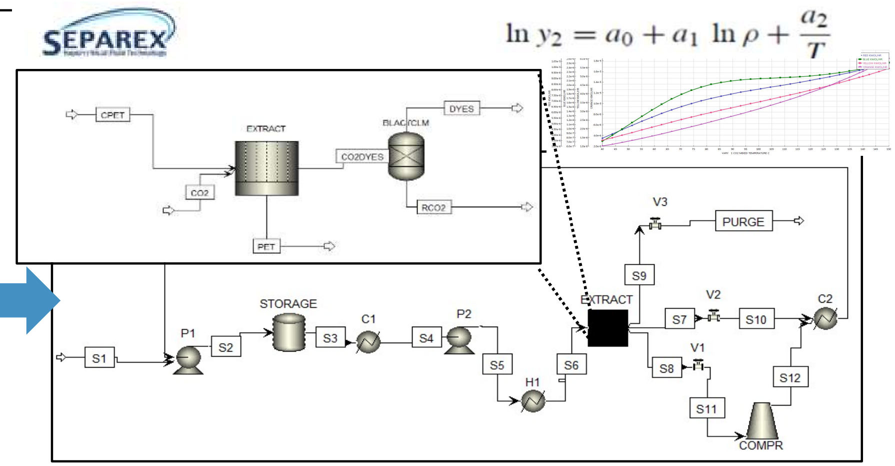
- End-users require products to be free of dyes, except peptides
- Processes must be put in order

Motivation

- Develop and include discolouration process
- Process order is dictated by process conditions

Phase 3: Cascade-discrete processing: corrected order & dye removal





SUPERCRITICAL CO2 EXTRACTION OF DISPERSE DYES FROM PET FIBRES

✓	PET fibres	×	Cotton fibres
×	PA fibres	×	Blend fibres

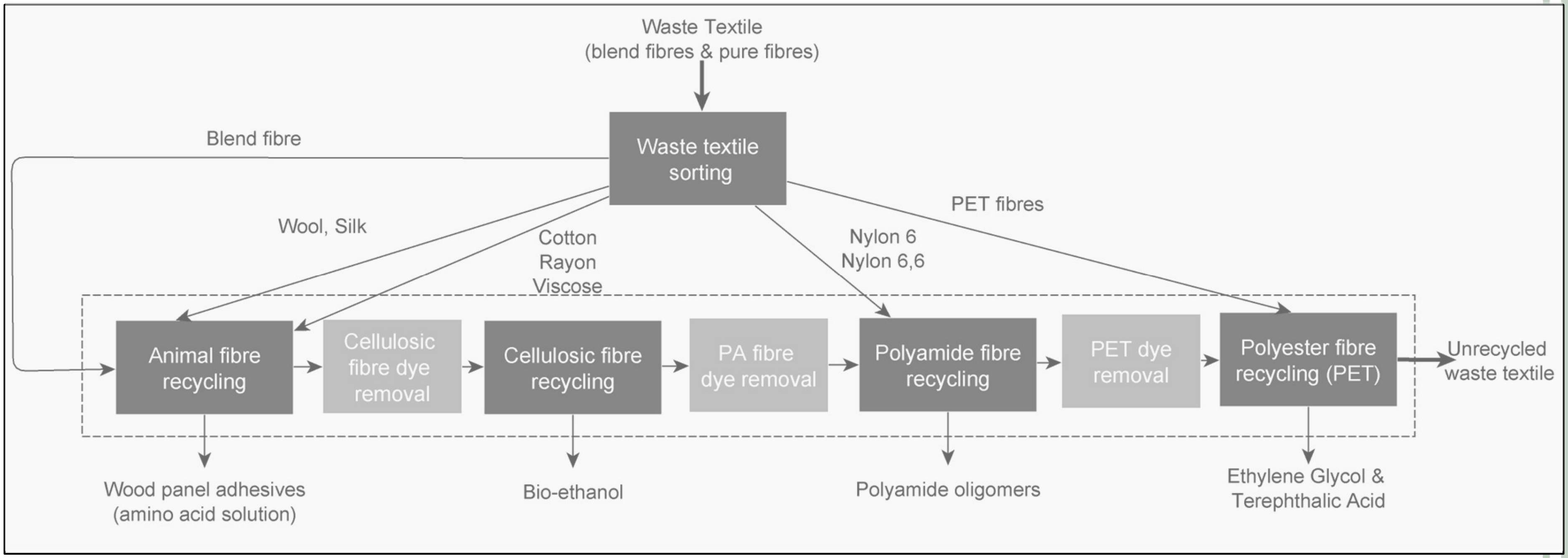
Challenge

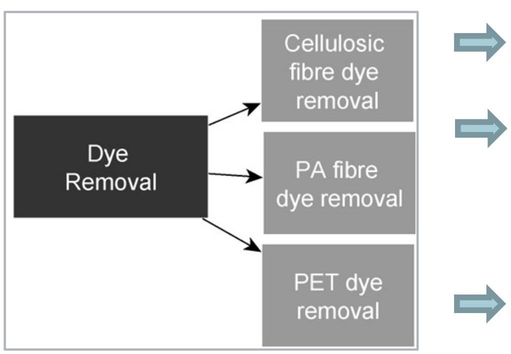
- One dye removal process does not achieve to discolour all waste textile

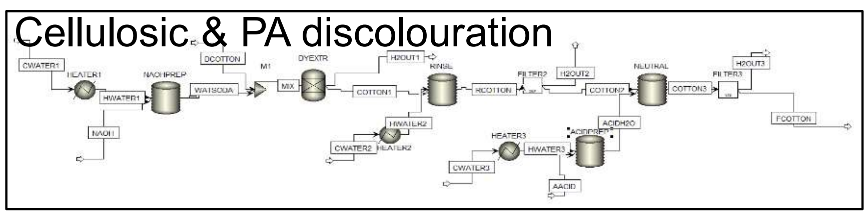
Motivation

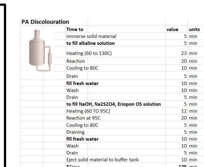
- Develop and integrate new discolouration processes

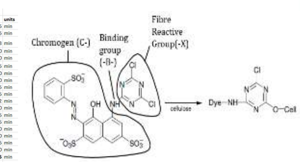
Phase 4: Cascade processing and 3 dye removal processes - 1

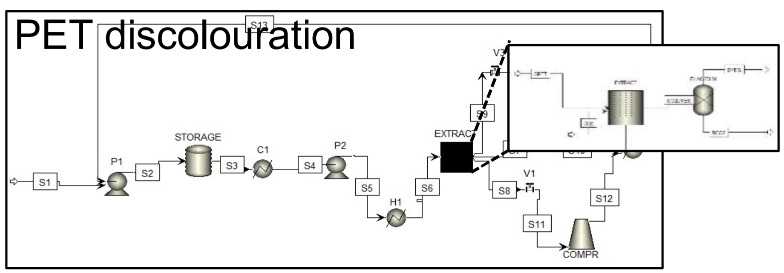


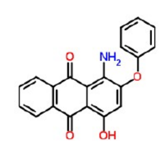




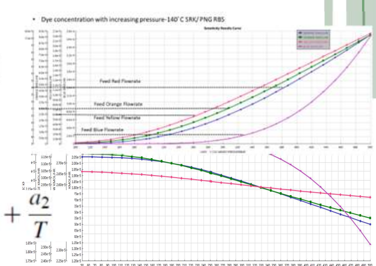




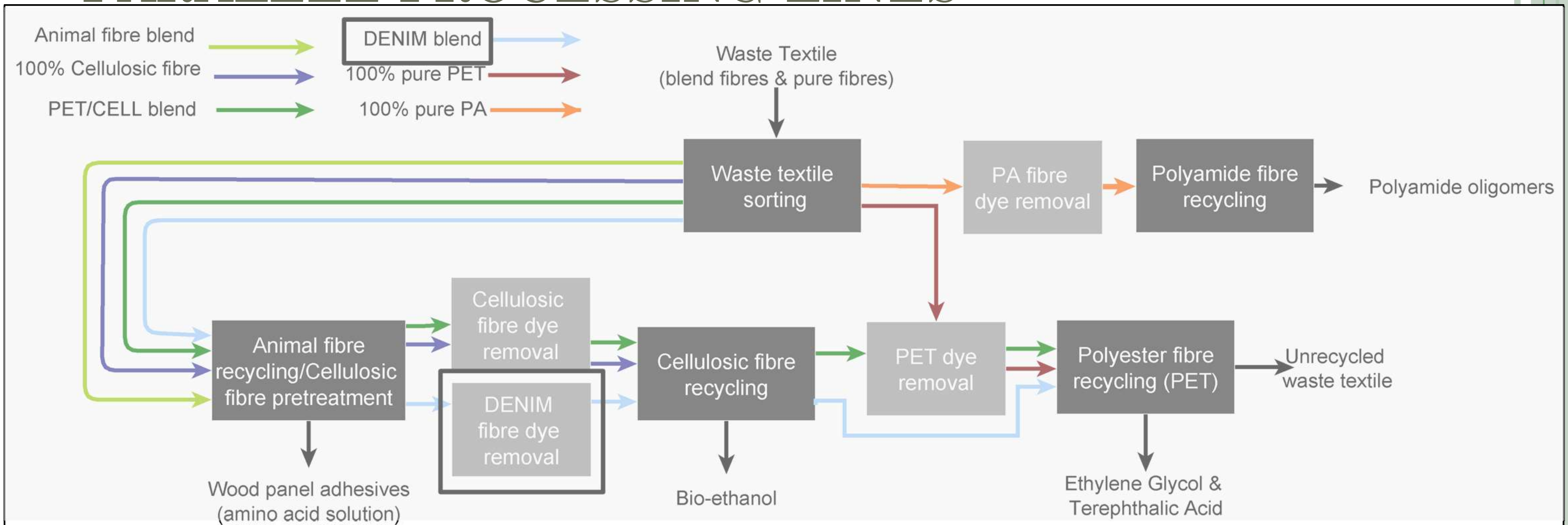




$$\ln y_2 = a_0 + a_1 \ln \rho + \frac{a_2}{T}$$



Phase 5: Cascade-discrete processing: parallel processing lines



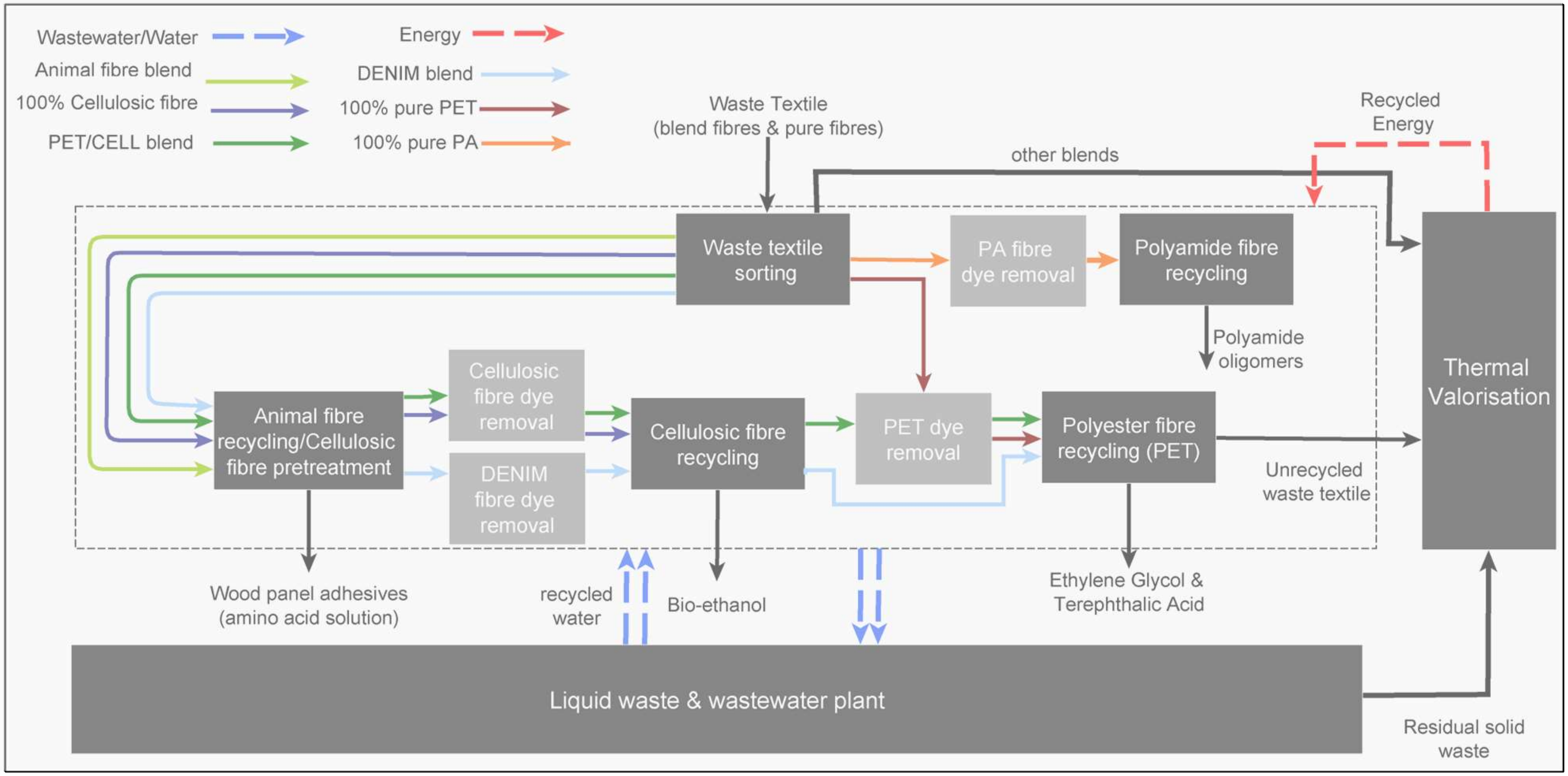
Challenge

- High capital costs & a lot of similar equipment required
- High utility costs: major water costs

Motivation

- Find ways to decrease costs in order to achieve sustainability and feasibility targets

PHASE 6: ADD ENERGY & WATER INTEGRATION



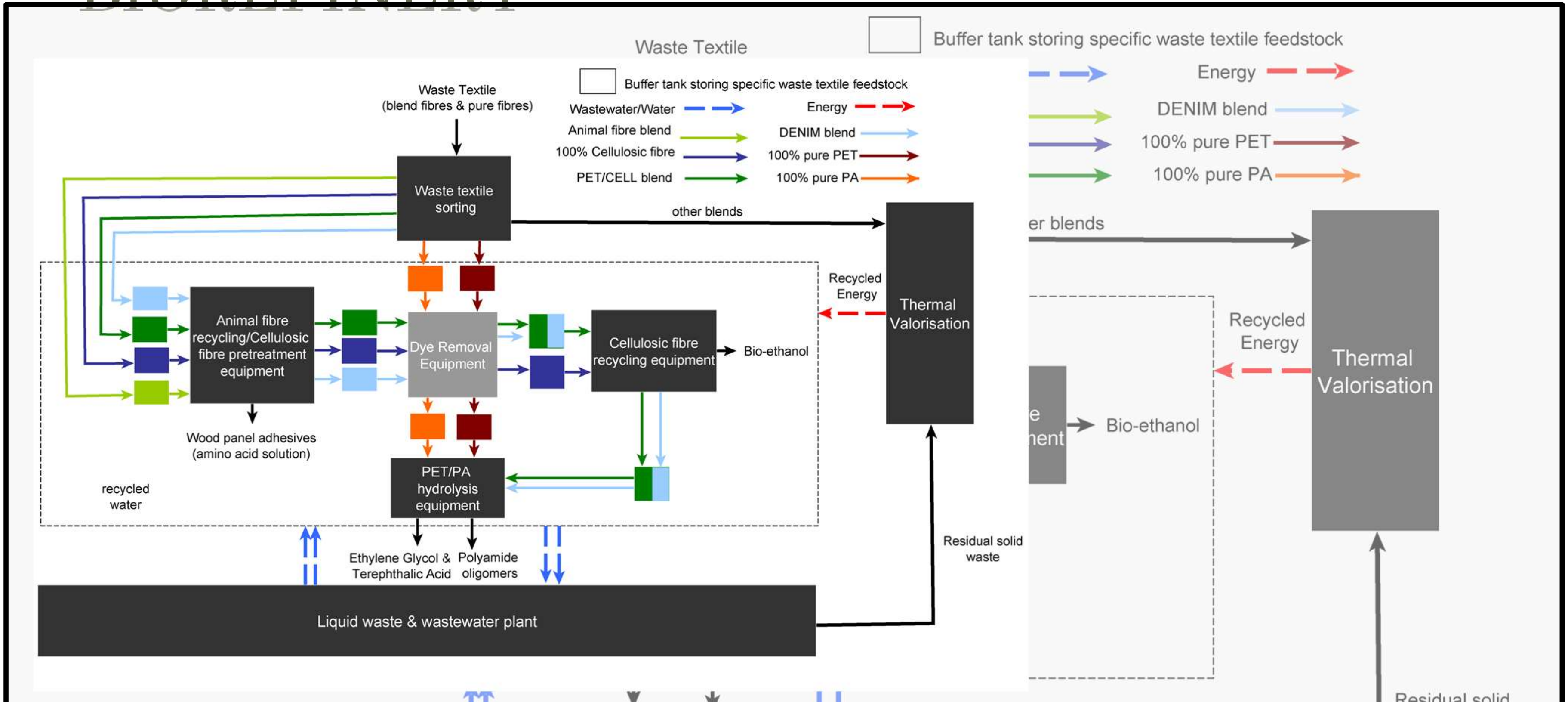
Challenge

- Operating costs are decreased but capital expenditure is still high

Motivation

- Find ways to decrease capital expenditure in order to achieve feasibility targets

Phase 7: Current waste textile biorefinery



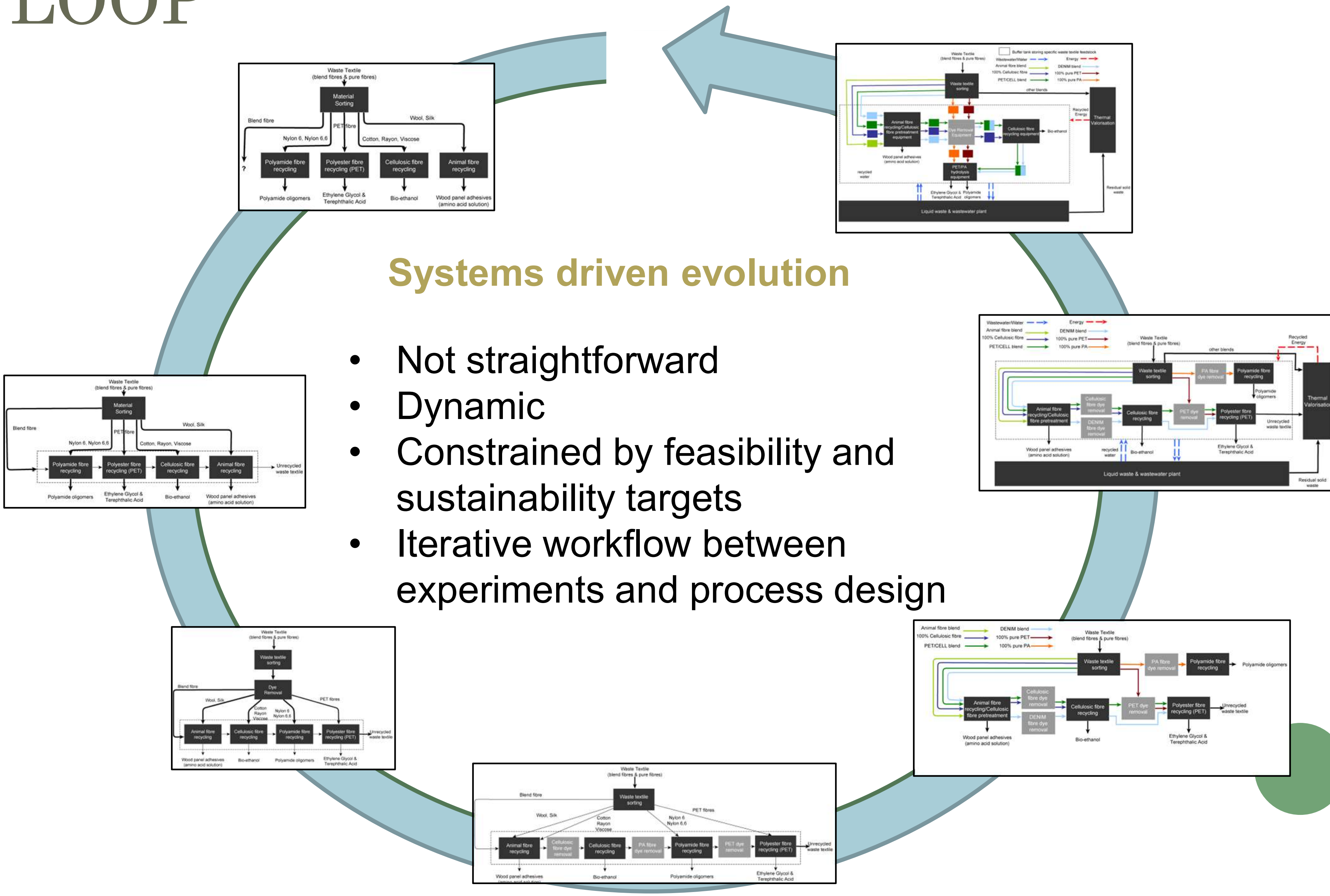
Challenge

- Equipment volume sizes are increased. Due to maximum standardized equipment, parallel units are designed.
- Complex batch scheduling & operation
- Complex utility integration with batch plant, challenging to recycle material

Motivation

- Simplify operational procedure
- Design a plant combining continuous and batch operations

THE EFFORT PATH TO CLOSE THE LOOP



Systems driven evolution

- Not straightforward
- Dynamic
- Constrained by feasibility and sustainability targets
- Iterative workflow between experiments and process design

Industrial symbiosis options

- Industrial symbiosis with **upstream flows**
  - Caustic soda
  - Cheaper alternatives for HCL
  - Water
- Industrial symbiosis with **downstream flows**
  - Glucose juice to 2G plants
  - Cellulose to 2G plants
  - Merge TA with virgin production
  - Merge PA with virgin production
  - Divert wastewater to nearby plants

Industrial symbiosis – upstream flows

Caustic soda

- high quality: 48% for PET hydrolysis (mainly) and PA hydrolysis;
- low quality: 52% of caustic for extrusion and discoloration
- symbiosis links: 2.8 M€/year

Sulfuric acid over HCL

- Good quality: neutralization of fibers (cellulose, denim, cellulose/PET, PET)
- Use of sulfuric acid: 3 to 4 times less expansive.
- If we replace 50% of HCL: 1.6 M€/year

Water

- Huge amount of water (24 t/h); 13% of utility cost (drinkable water 1.7 €/m^3).
- Use industrial filtered water in more than half of the volume (e.g. discoloration and first washing step after discoloration).
- Cost lowered by a factor of 2. 1.7 M€/year savings

Industrial symbiosis – downstream flows

Sell diluted **glucose**

- Condensation of glucose is expensive. Transfer 10% glucose (e.g. to nearby fermentation plant at 100 km).
- Energy savings: 1.2 M€/year, fixed costs reduction: 5.6 M€, additional transport costs 1.8 M€. <u>Savings: 5 M€/y</u>.

Share selected **cellulosic streams**

- New technology upgrades cellulose (cotton, denim) initially unsuitable since:
  - impurities (metals, elastane, fossil polymers);
  - physical properties different from woody residues;
  - dyes and additives detrimental to fermentation
- Now possible to share
  - CAPEX annualization savings <u>8M€/year</u>

Industrial symbiosis – downstream flows (2)

Terephthalic acid

- r-TA challenge: is quality (purification is expensive)
- Symbiosis with virgin producers: mix r-TA with fossil TA; 4 PTA plants (350-950 kt/year): easy to absorb r-TA (8.5 kt/year)
- Regulations may promote the blended product (as in biofuels)

Polyamides

- Low Volumes (600 t/yr, 250 t/yr CL and AA; EU in 20-800kt); r-PA in place (Aquafil 12 kt/yr)
- send r-PA to existing units; <u>savings</u>: several hundred thousands (low)

Wastewater

- wastewater (several process lines) to manufacture phenolformaldehyde resin and particleboards without loss of properties
- limited scope for savings

Industrial symbiosis saves the case

	Free cash flow (M€/year)	Improvements of free cash flow vs base case (M€/year)	CAPEX for 80 kt/year (M€)
Base case: 1 x 80 kt/year centralized chemical plant producing 80% glucose juice	-25		207
Decentralized chemical plants (3 x 27 kt/year)		-8	304
New textile feedstock for Resyntex plant 1 x 160 kt/year centralized plant		+6 (for 80 kt)	162 (for 80 kt)
Symbiosis with 2G ethanol plant Resyntex chemical plant at the door of 2 G ethanol plant		+8	93
Resyntex chemical plant at the door of ethanol or lactic acid plant		+7	104
Better value for glucose juice (2G ethanol or lactic acid)		+4	
Symbiosis with a low cost caustic soda producer		Up to +2.5	
Partial replacement of hydrochloric acid by sulfuric acid		+1.6	
Partial substitution of demineralized/tap water by industrial filtrated water		+1.7	
Extended producer responsibility fee on new clothes corresponding to 0.1€/kg textile waste to be chemically recycled		+8	

Positive cash flow!

Additional incentive needed to **justify CAPEX**.

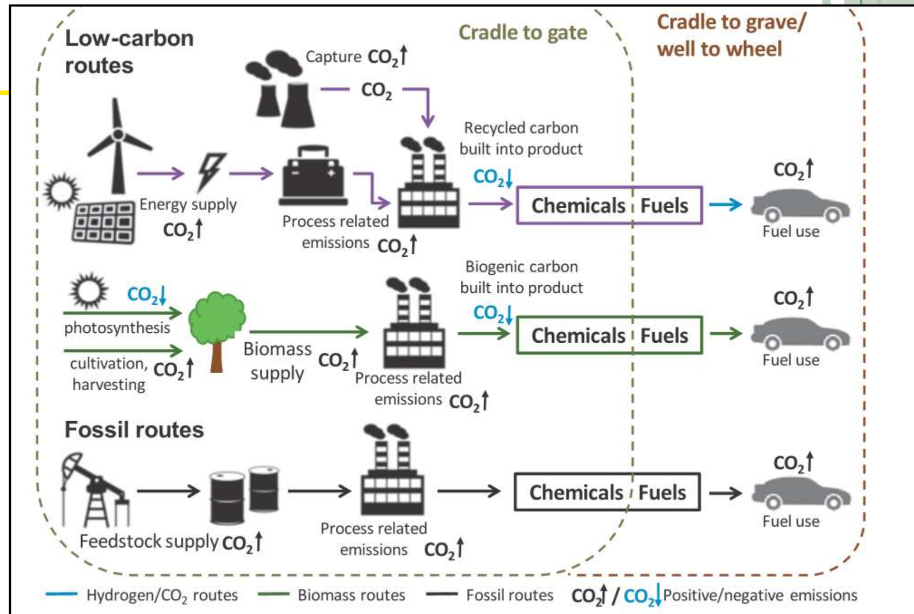
CROSS-INDUSTRIAL COLLABORATIVE CHAINS -

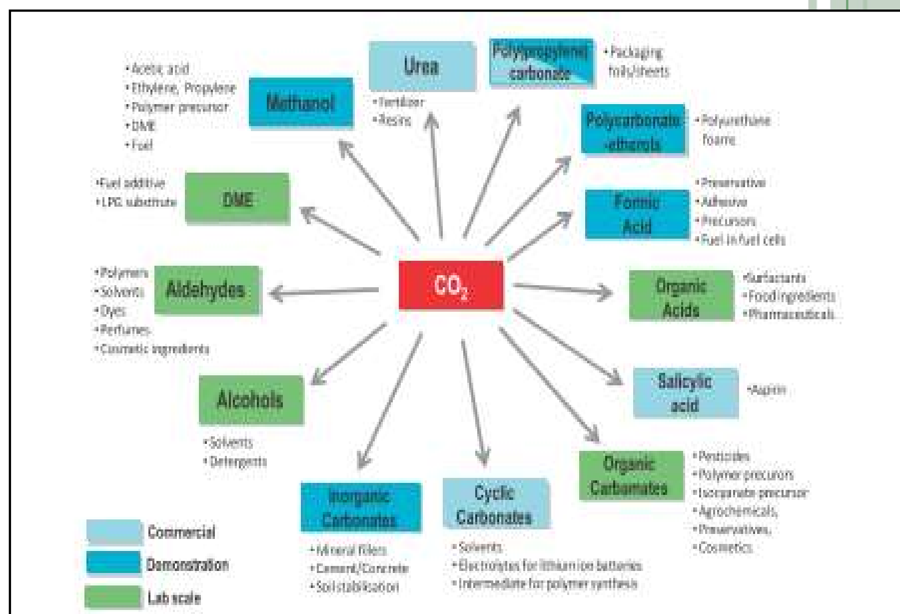
BIOBASED INDUSTRIES AND THE BIG PICTURE

VALUE CHAINS USING CO2

- Emissions reduction: 210 Mt/yr (2050)
- 70 Mt - best practice, reengineering
  - Process and energy integration
  - Process intensification
- From CCU to CO2 valorization
  - methanol (CO2, H2)
  - Ethylene/propylene (through CH_30H)
  - BTX (via CH30H)
  - Synthetic fuels (many)
  - Upgrade CH4/CO2 mixtures to fuels
- Innovative solutions
  - Integration of bio and chemical paths
  - Novel chemistries
  - Reactive separation systems

  (membranes, extraction, solvents etc)

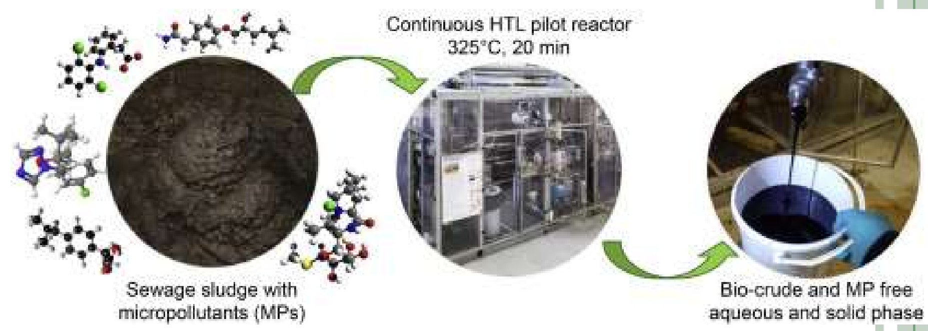


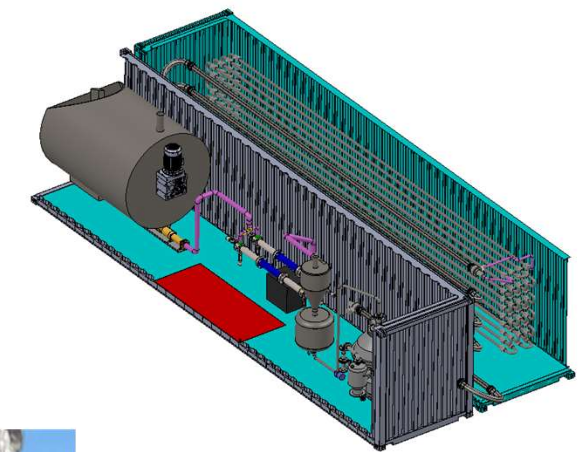


2018, Dechema/CEFIC, Technology Study, Low carbon energy and feedstock for the European Chemical Industry

Biodiesel from sludge

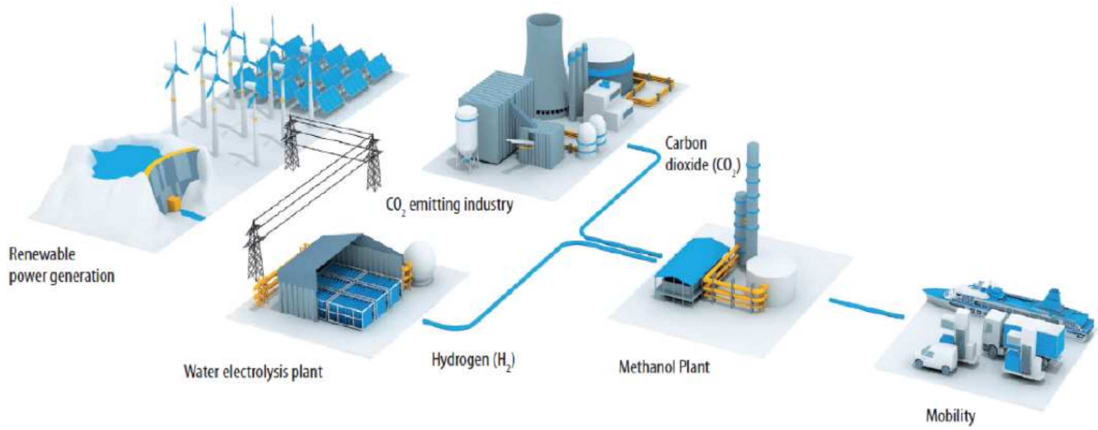
- Hydrothermal liquefaction of a wide range of feedstocks
- Continuous processes since 2015
- Larger units 1 barrel/minute. Cost €20-50 million
- Smaller compact units for local use (30,000tn/hr) in 2x40’ containers/ Cost from €2-5 million
- Excellent prospects to integrate with oil refineries

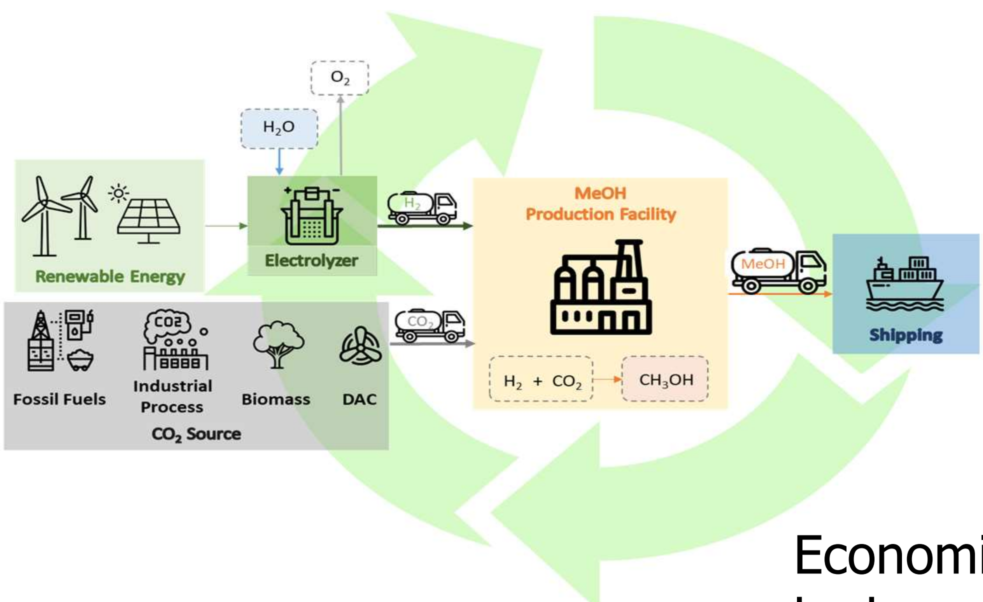


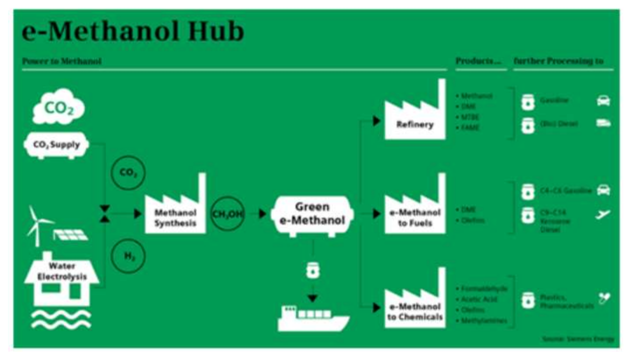


PRODUCTION OF E-FUELS

THYSSENKRUP PROJECT

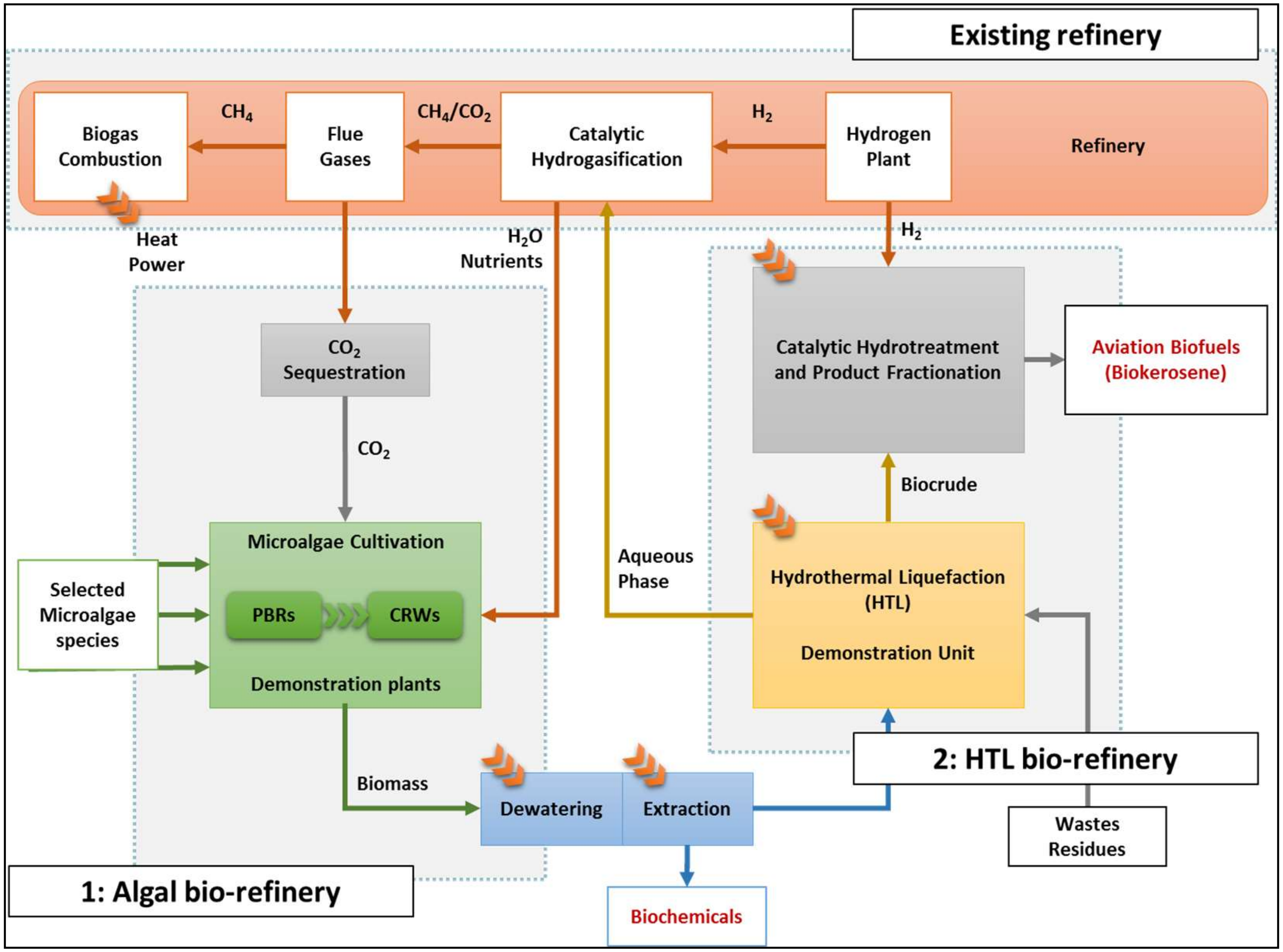






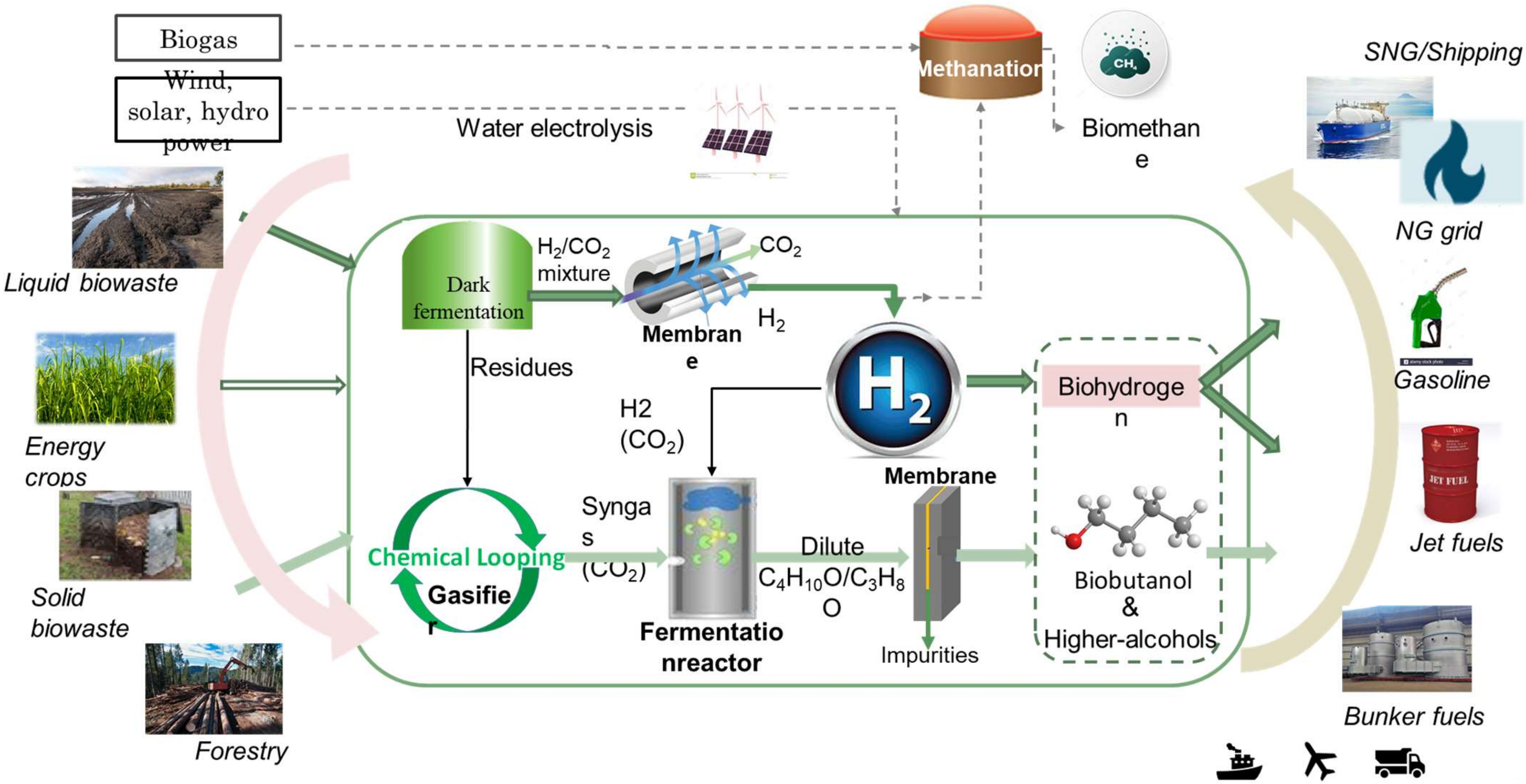
Economics of e-fuels combine costs of hydrogen, e-fuel production, carbon dioxide capture, end-fuel processing, storage and distribution.

CROSS-INDUSTRIAL CHAINS - REFINERIES



Industrial symbiosis beyond straightforward sink-to-source matches

CROSS-INDUSTRIAL CHAINS - HYDROGEN



Production of H2 for either feedstock or fuel

Emerging data-driven challenges for model and systems intelligence

MODEL AND SYSTEMS INTELLIGENCE

- **Data analytics, semantics and AI**
  - High-throughput analysis - semantics and ontology engineering could automate and coordinate experiments
  - Digital twinning – Types of models
    - Significant volumes of data in the absence of strong or clear underlying principles
    - Computational expensive models (e.g. property models)
    - Data embedding on existing physical models
- **Applications**
  - **NLP to optimize experiments** e.g. high-throughput simulation and optimization
  - **Process intensification** e.g. for innovative process equipment
  - **Model intelligence** e.g. connect curated properties and kinetics with real-life experiments
  - **Ex-ante analysis**

Semantics for systems automation (Optimization for the layman)

Examples from bioenergy

- *What is the **potential** to **install** a biogas plant in **Texas?***
- *What **product portfolios** would be most **profitable** in **my** plant?*
- *What is the **best waste treatment** technology to use?*

Examples from waste and energy management

- *How to valorize **scrap metals** from **shipyards**?*
- *What is the cheapest energy source for my plant?*

How to link conventional problem descriptions with natural language?

Basic idea

- Establish <u>vocabularies</u> to relate words (concepts) with methods, then models, data, information and knowledge
- Produce <u>vocabulary properties</u> to automate

Vocabulary-based concepts

- Problem description concepts
  - Problem description aspects (as in conventional model)
    - Units, specs, application domain
    - Selection criteria eg profit, cost, combinations
- Background and Tacit knowledge
  - Triggered by problem concepts but modeled independently of the problem
- Model concepts
  - Multiple models, multiple translations
- Results, analysis
  - Results, visual aids, validation (possible by other models eg simulation)
- Most concepts relate to each other

ILLUSTRATION

Problem Concept
Tacit Knowledge (language related)

What is the Potential to Profit from Agricultural Residues and Municipal Solid Waste in Teeside?

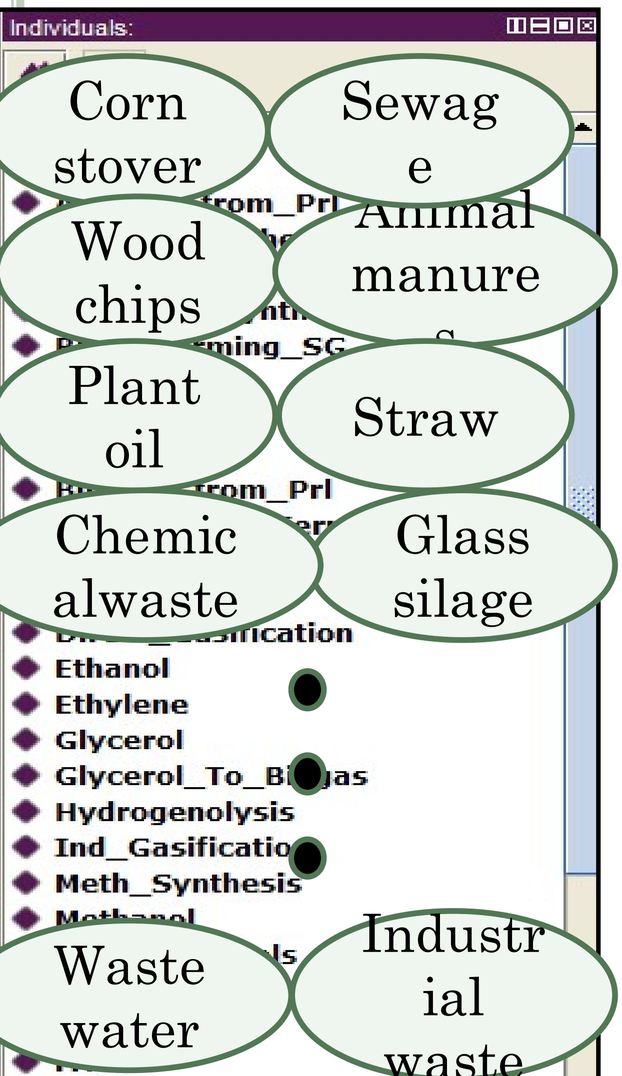
Problem Concept
Model concept (synthesis)

Problem Concept (supply)
Tacit Knowledge (ME models, cost models, LCA, chemistries)

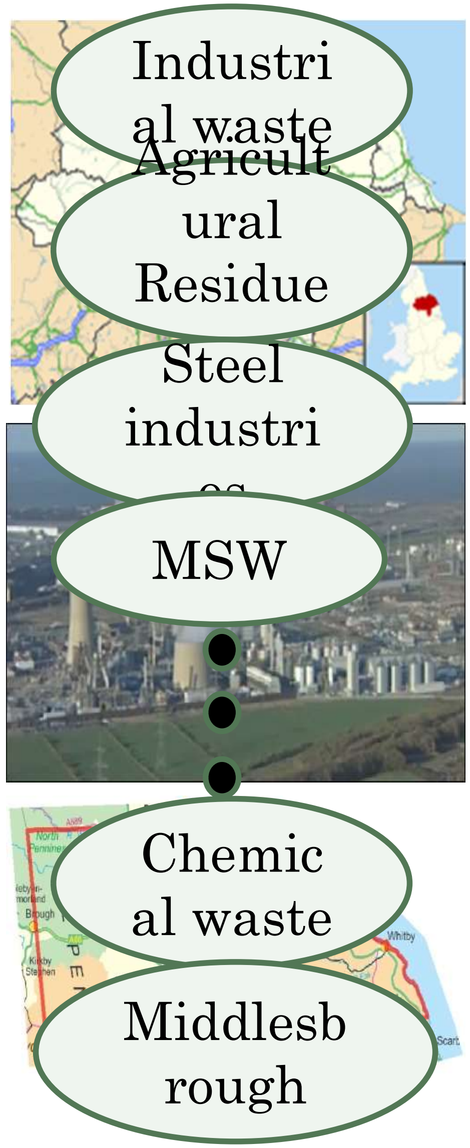
Tacit Knowledge (supplies, location)

Use ontologies to share data in relation to each one of the above

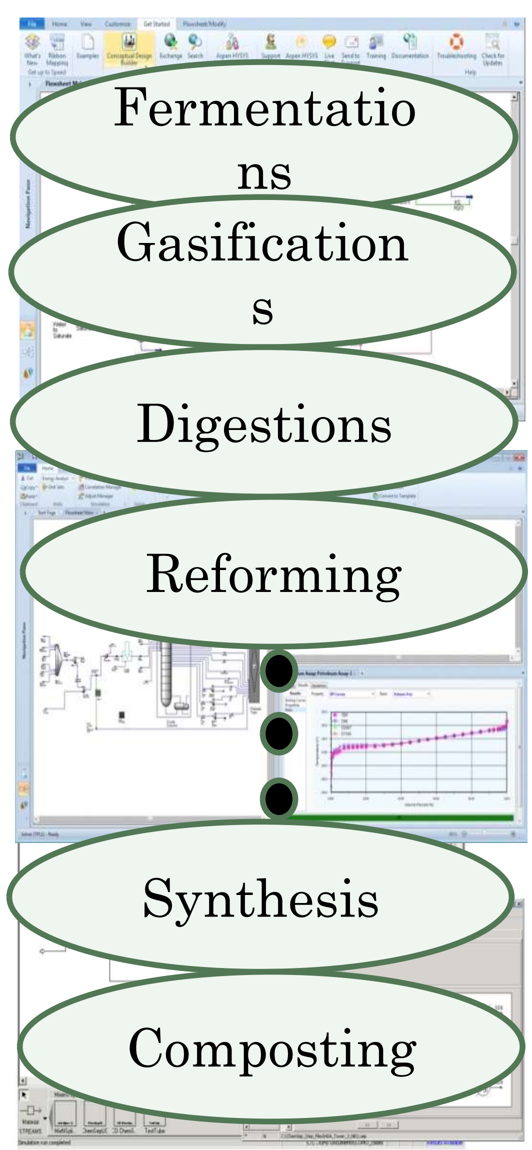
PROBLEM AND BACKGROUND CONCEPTS



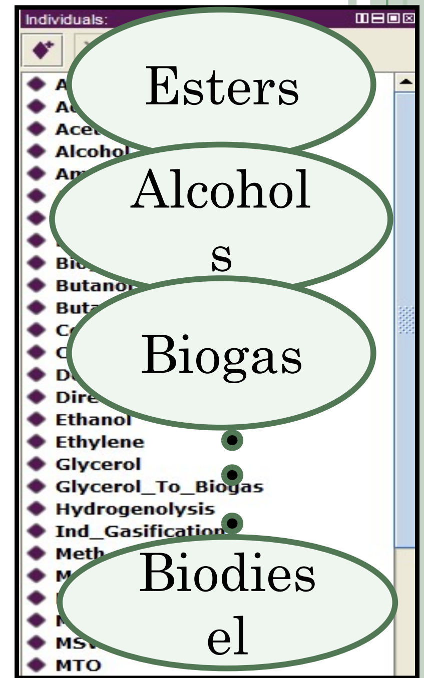
Agricultural Residues and MSW



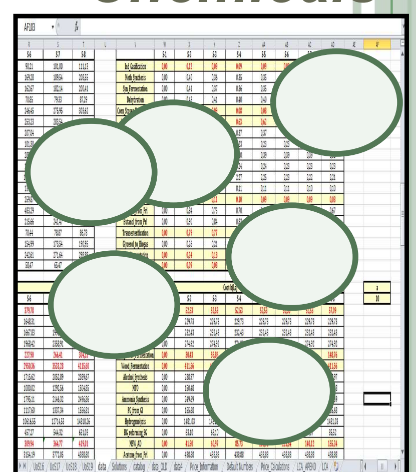
Teeside



Technologies

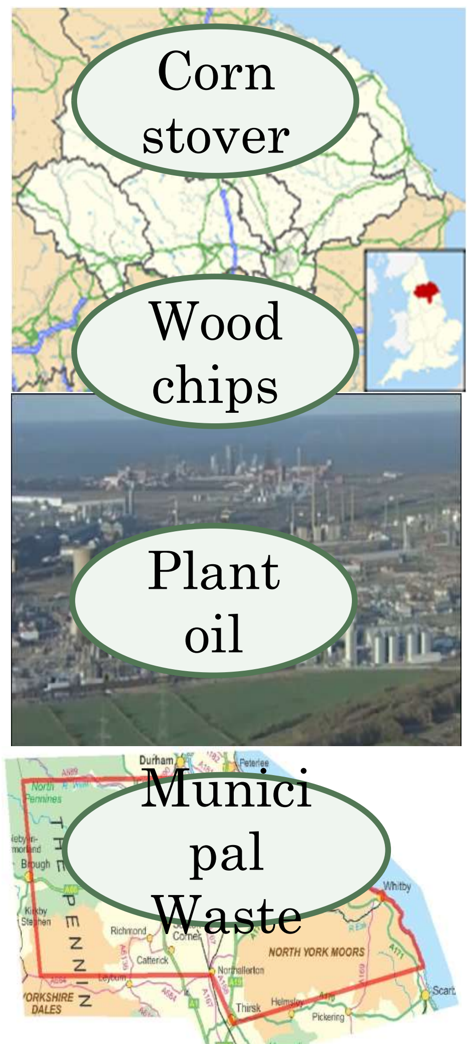


Chemicals

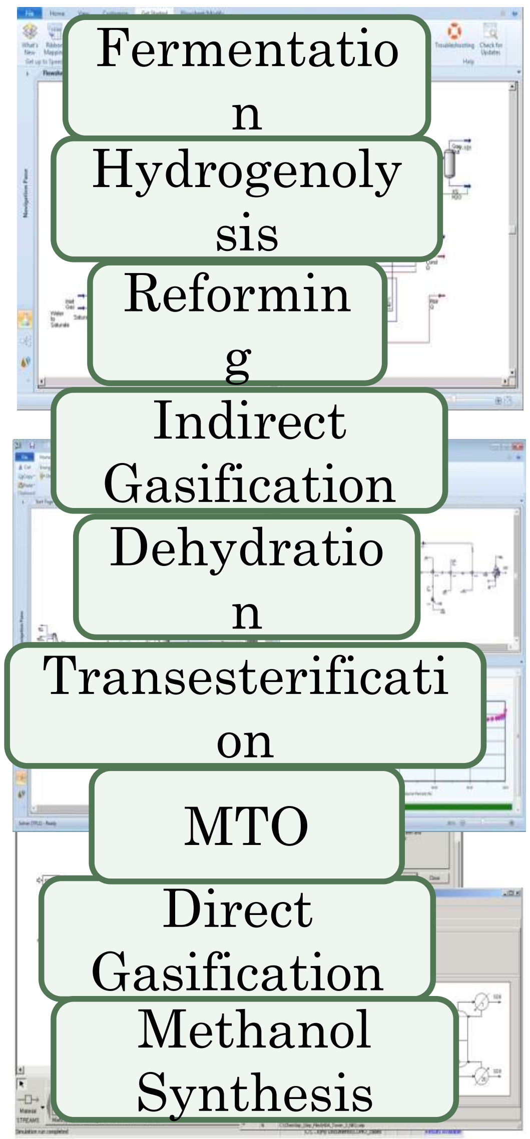


Cost models

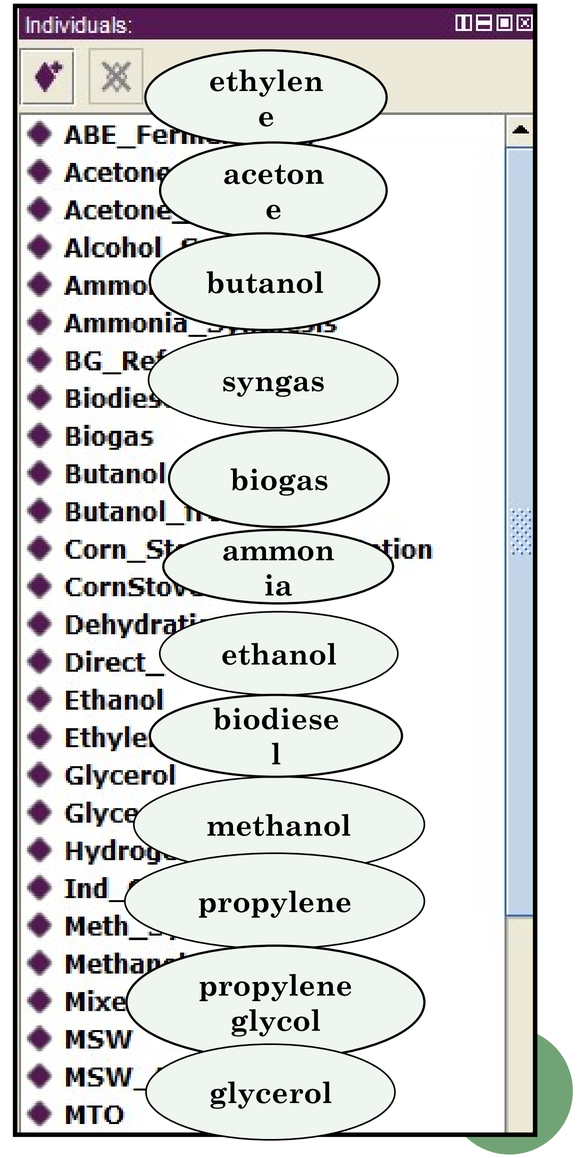
Ontology components



Agricultural Residues and MSW @Teeside

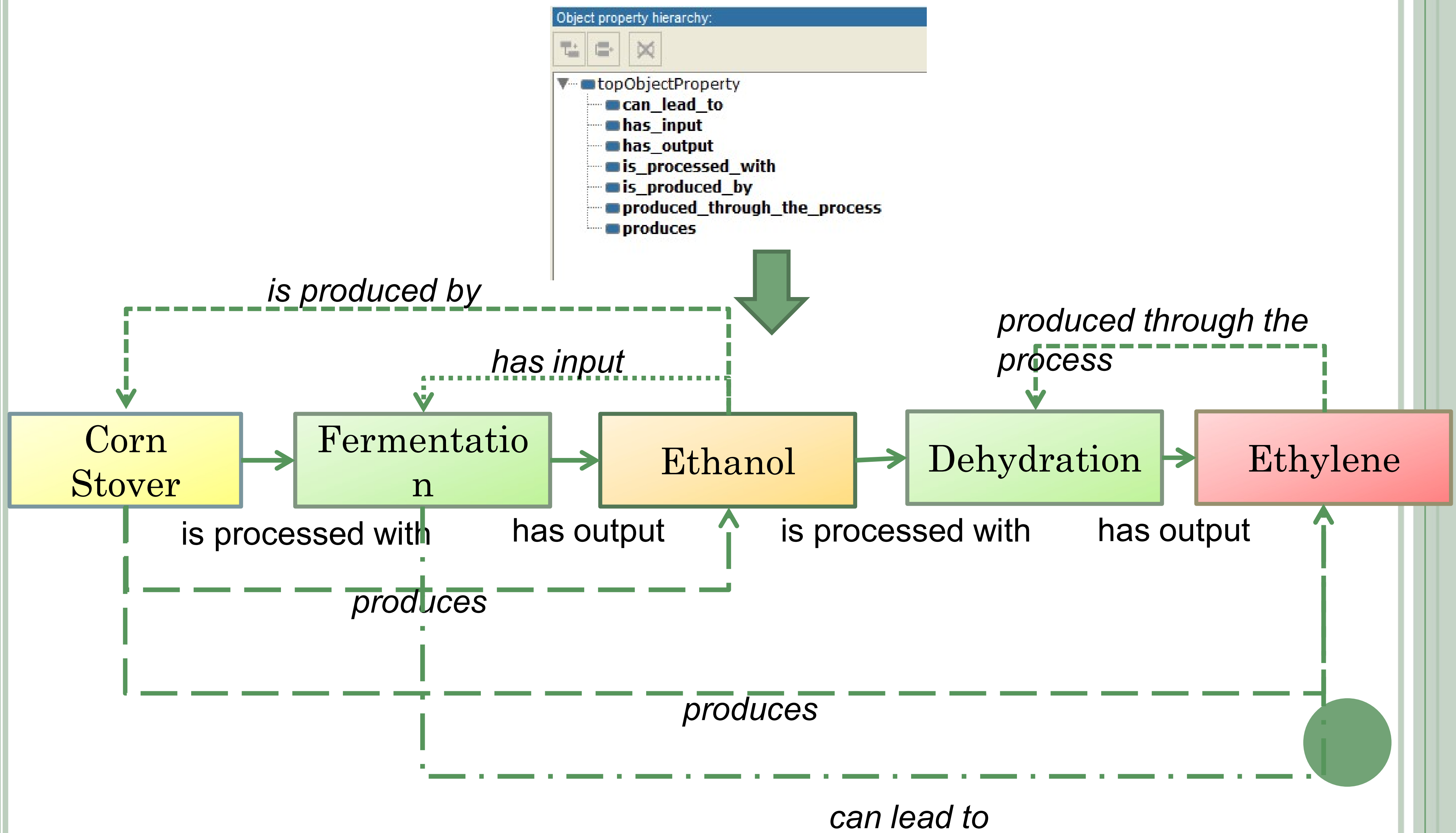


Related technologies

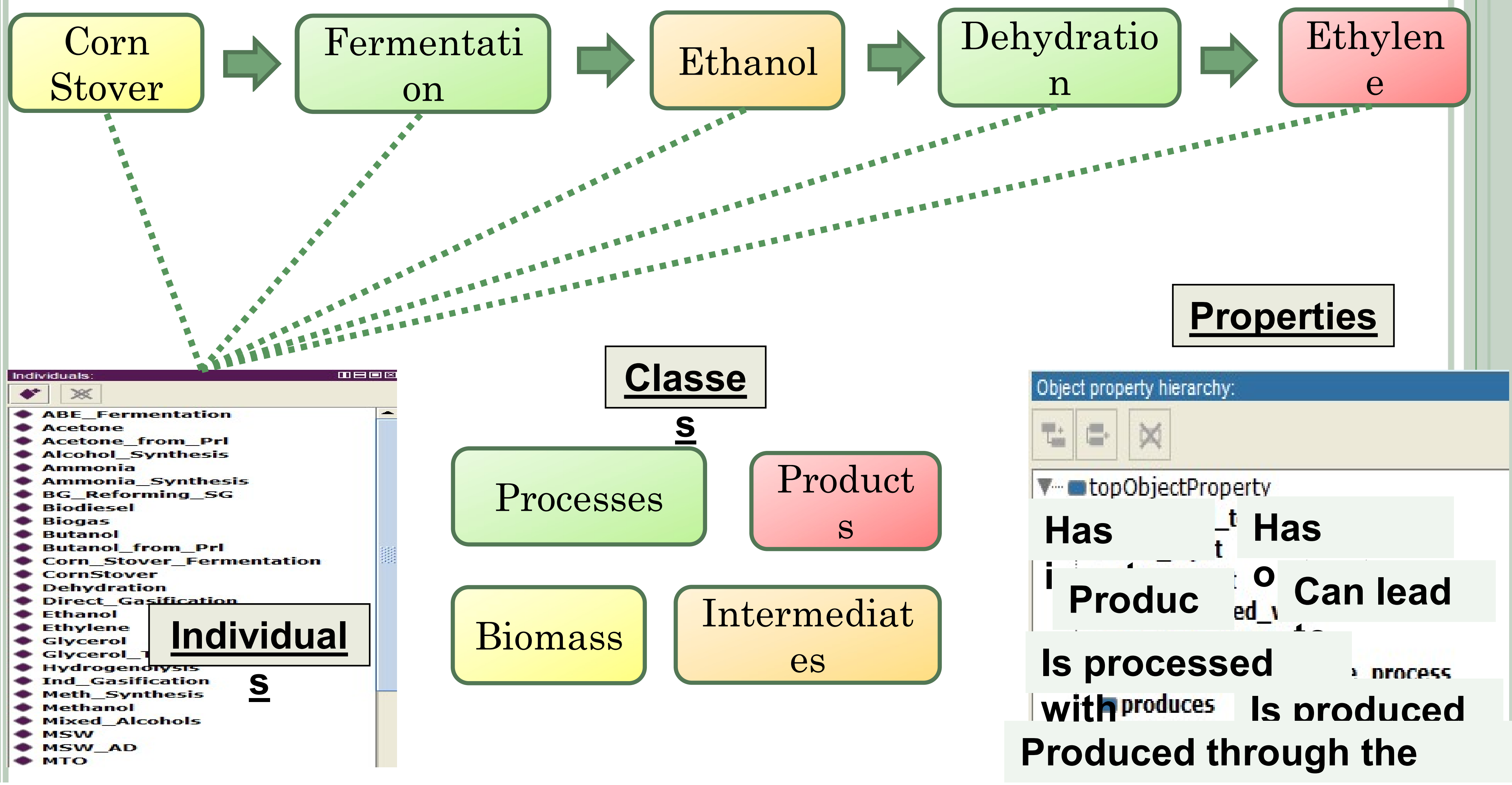


Related valorization paths

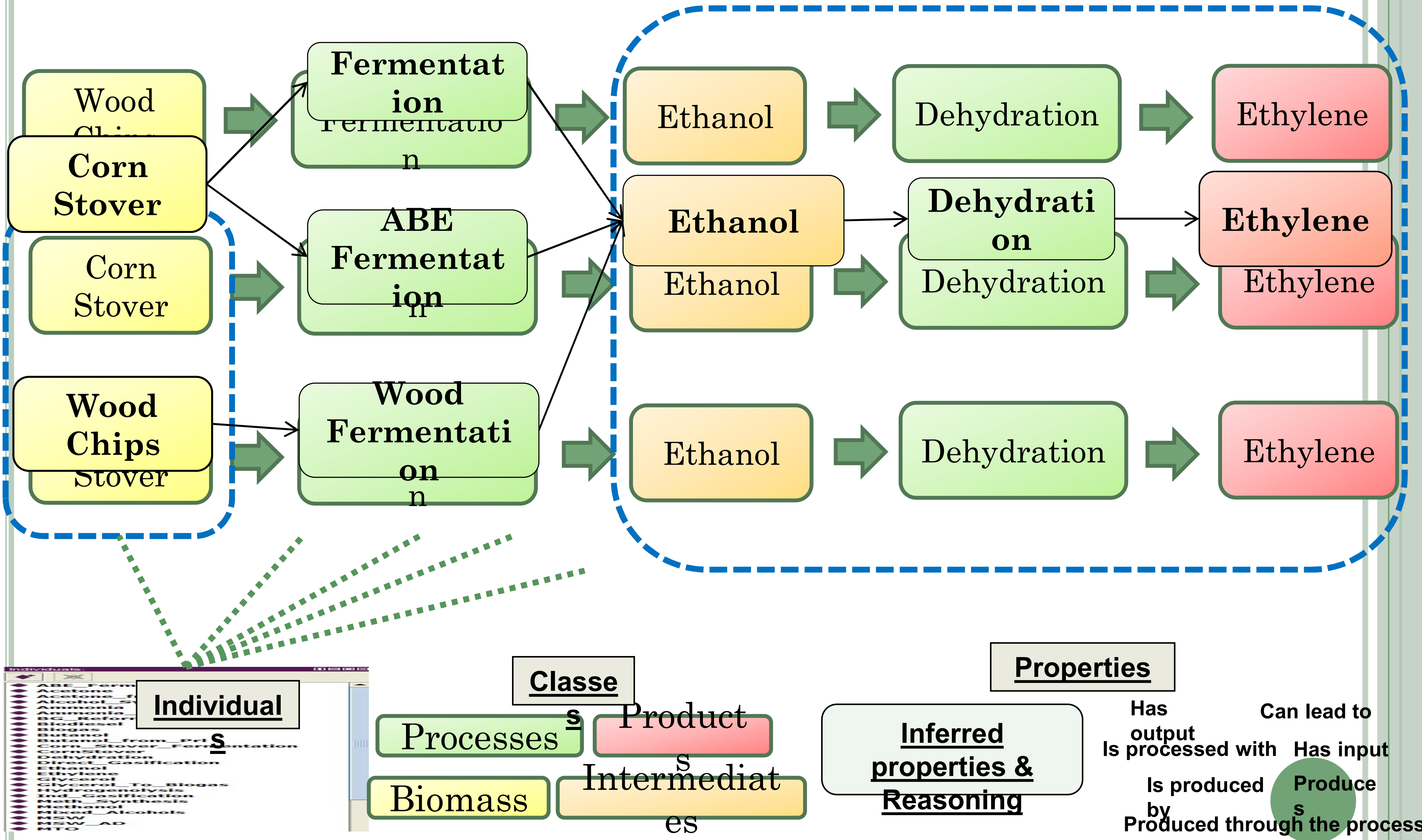
Concept properties and associations

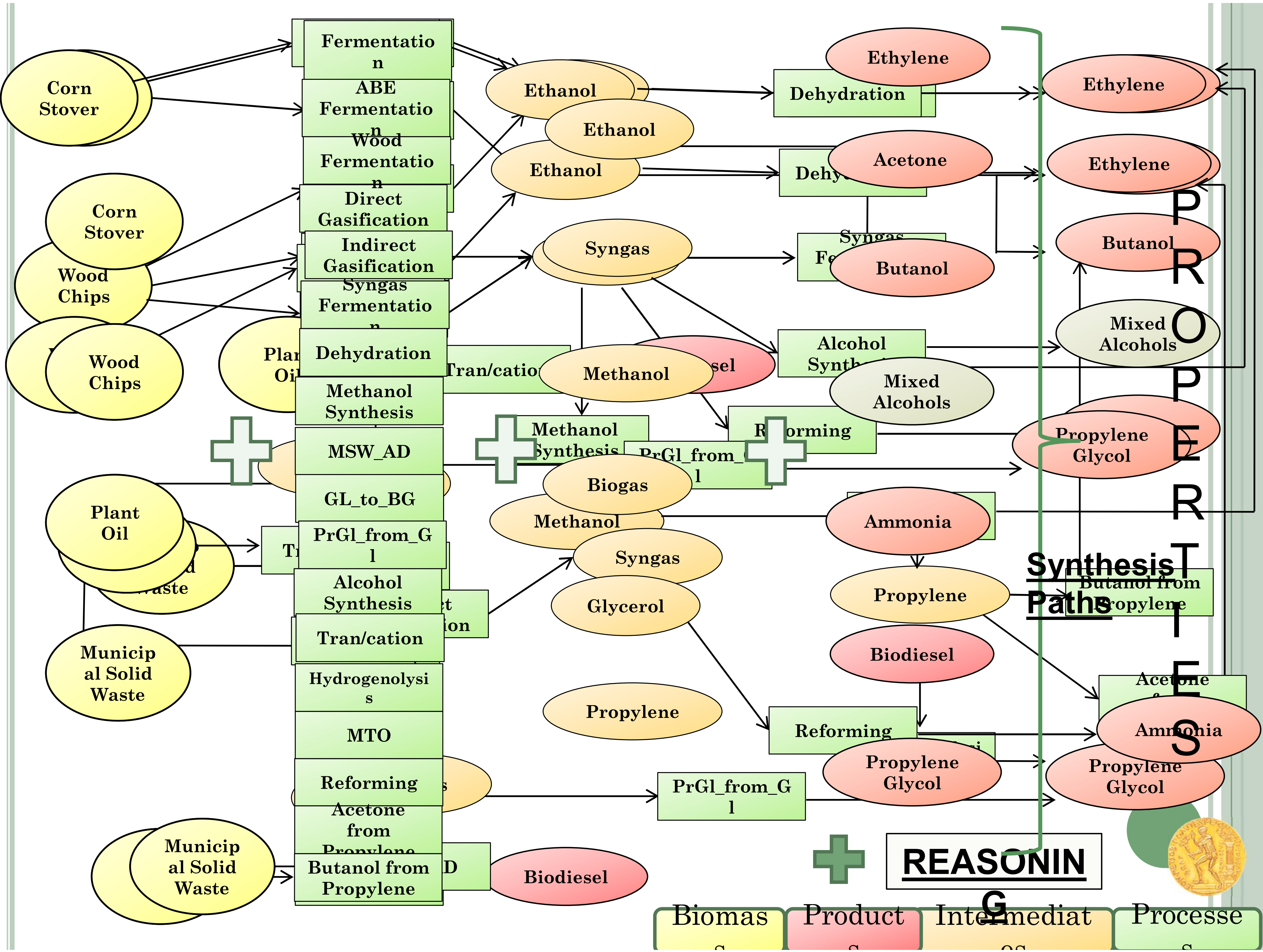


BUILDING SYNTHESIS PATHSR



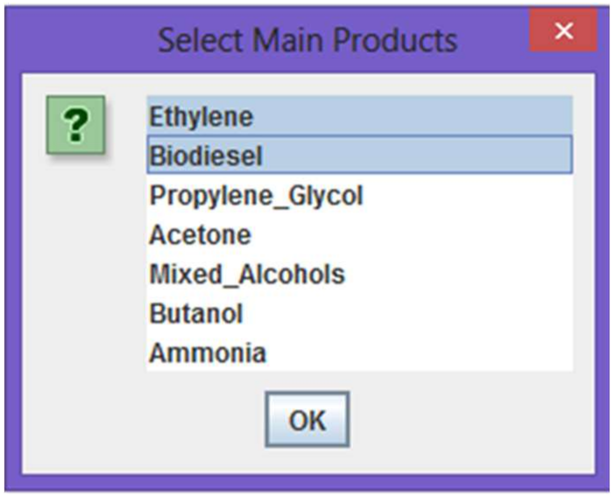
Integrating paths and superstructures

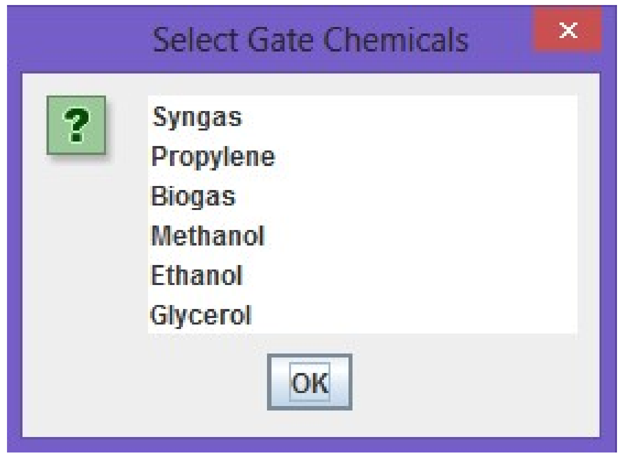



Corn Stover
Wood Chips
Plant Oil
Municipal Solid Waste
Fermentation
ABE Fermentation
Wood Fermentation
Direct Gasification
Indirect Gasification
Syngas Fermentation
Dehydration
Methanol Synthesis
MSW_AD
GL_to_BG
PrGl_from_Gl
Alcohol Synthesis
Tran/cation
Hydrogenolysis
MTO
Reforming
Acetone from Propylene
Butanol from Propylene
Ethanol
Syngas
Methanol
Biogas
Glycerol
Propylene
Biodiesel
Ethylene
Acetone
Butanol
Mixed Alcohols
Propylene Glycol
Ammonia
PROPERTIES
Synthesis Paths
REASONING
Biomass
Products
Intermediates
Processes

Ontology-free front end

- User interface to hide ontologies and process/background and model concepts





- Advanced options for later development
  - Ontologies: end-user management
  - Model library management (editing, import/export)

JAVA IMPLEMENTATION (2)

- Generates GAMS code on the fly with options to run or store
- Potential to create massive libraries of models with different functions

```
*************************************Sets***********************
$onempty
ac          "all chemicals"  /inlet, cornstover, woodchips, MSW,
j(ac)       "raw material"   /cornstover,woodchips/
i(ac)       "gate chemical"  /syngas,ethanol,methanol,propylene/
k(ac)       "all products"   /ethylene,syngas,ethanol, mixed_alc
mp(k)       "main products"  /ethylene,syngas,ethanol/
bp(k)       "by products"    /mixed_alcohols/
l           "processes included in the case study" /corn_stover_
*********************************Connections******************
```

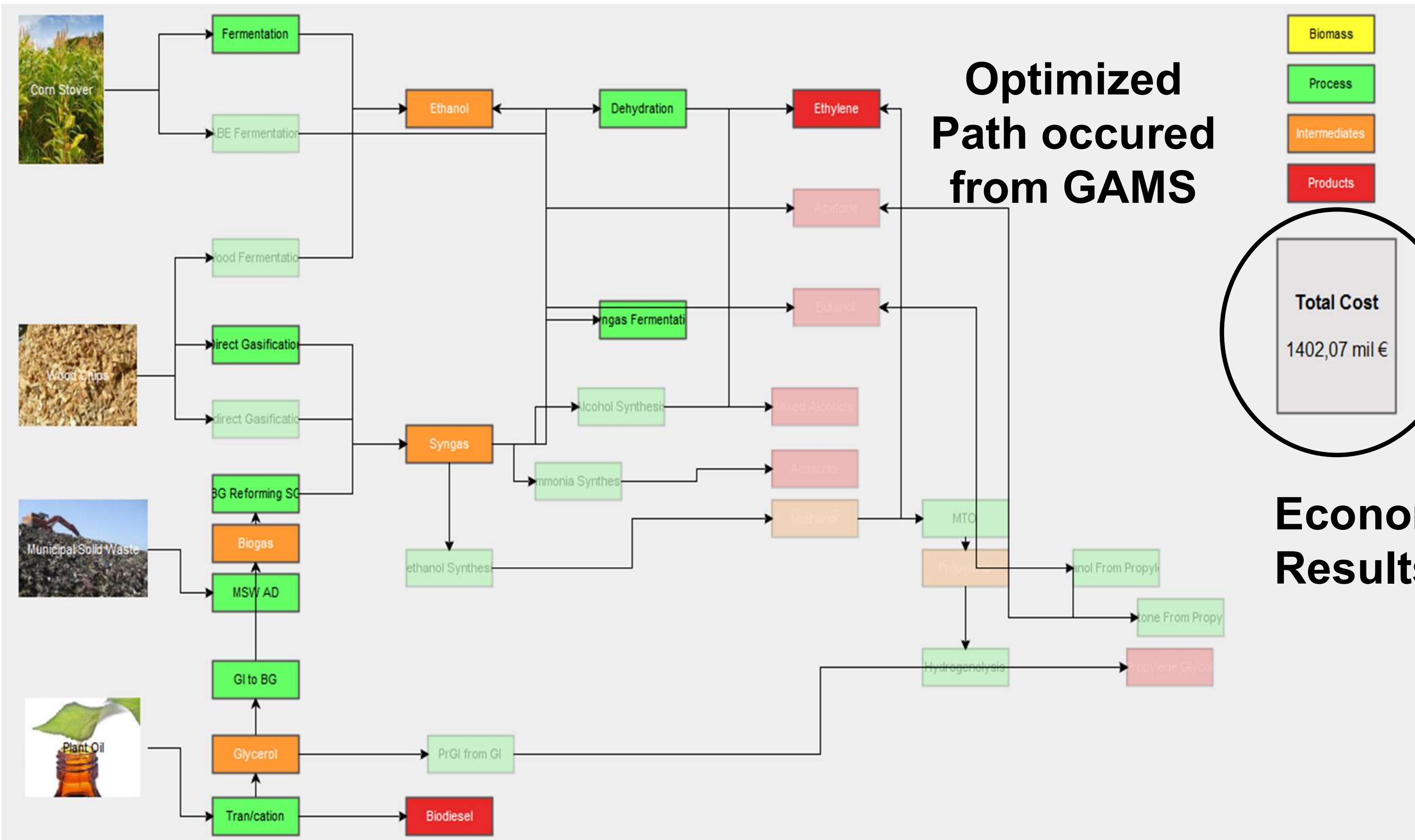
Scenario-Solution.gms

```
bp(k)       "by products"    /mixed_alcohols/
l           "processes included in the case study" /corn_stover_fermentati
*********************************Connections***************************

*****************************DownStream Processes**********************
******************Raw Marerials to Downstream Processes****************
downstream_rm(j,l) "connections of raw materials with the down stream prc
           / cornstover.(corn_stover_fermentation)
             woodchips.(wood_fermentation,ind_gasification,direct_gasific
*****************Gate Chemicals to Downstream Processes****************
downstream_gc(i,l) "connections of the gate chemicals with the down strea
           /ethanol.dehydration
            syngas.(syn_fermentation,alcohol_synthesis)
            methanol.(MTO)/
```

- Work to present jointly with GAMS at next INFORMS

VISUAL REPRESENTATION OF RESULTS



Economic Results

DEMO

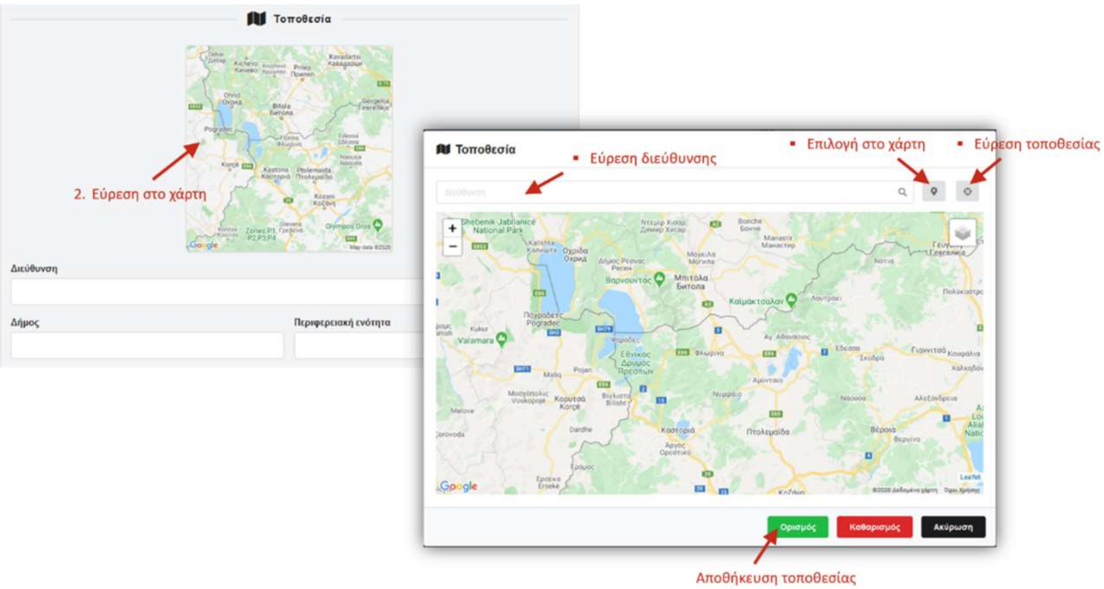
Semantically enabled synthesis

- Selecting raw materials, products and intermediates as products

http://www.reneseng.com/index.php/structure/demos

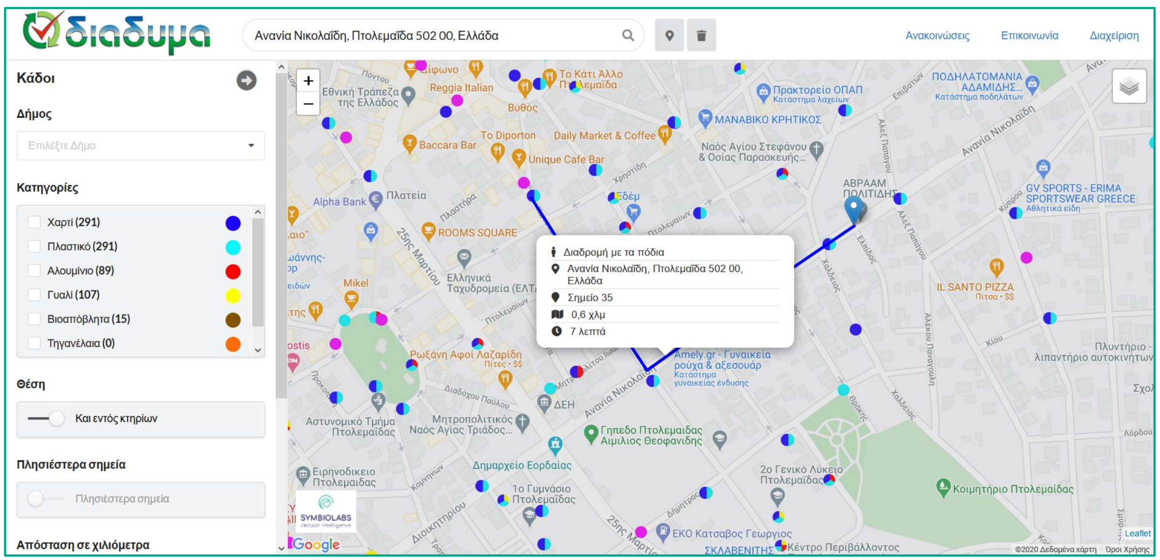
Data modelling as a service

ATHENA
Research & Innovation
Information Technologies



SYMBIOLABS
circular intelligence

- Spin-off with ATHENA
- Bio-energy platforms integrated with GPS and waste collection
- Services to prefectures, regional development agencies, process industries
- Digital services extend to applications to digital twinning



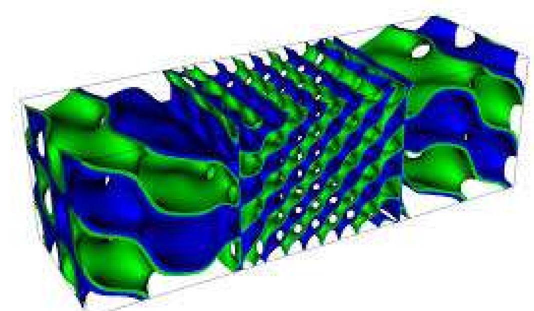
SymbioICT μμAI διαδυμα TITAN GREECE

Process intensification - additive manufacturing

Kenics® KMX-V Static Mixer

- Combine PSE, CAD, CFD to customize design
- Chemical reactors and mixers [1-4]
  - Innovative design – chemistry based equipment desing
  - Less material, better heat transfer (e.g. zig-zag design), smaller pressure drops, reduction in residence times
  - Εφαρμογές – καταλυτική οξείδωση αλκοολών, παραγωγή μεθανίου από CO2

- Distillation [5]
  - Integrated stage design, efficient packing and stage efficiency
  - Less material, energy savings, less operating cost
  - Applications – RPB: cost improvements by 2 orders of magnitud



- Membranes [6-7]
  - Innovating designs adjusted to the mixtures at hand
  - Additive materials (spacers), to differentiate pores
  - Applications – pressure reduction by 7.5, in CO2 transfer

[1]. 2 Hurt et al. Catal. Sci. Technology, 2017; [2]. Danaci et al., Cat Today, 2016, 273: 234-243; [3]. Ghanem et al, Chem. Eng. Res. Des. 2014, 92: 205-228; [4]. De Vries A. 3D-printed metal flow reactors and mixers, RSC symposium, 2017, Munich; [5]. Neuman et al, Chem. Eng. Res. Des. 2018, 134: 443-462; [6]. Gu, Adjiman, Mem. Sci., 2017, 527: 78-91; [7]. Fritzman et al., Membr. Sci., 2013, 446:189-200;

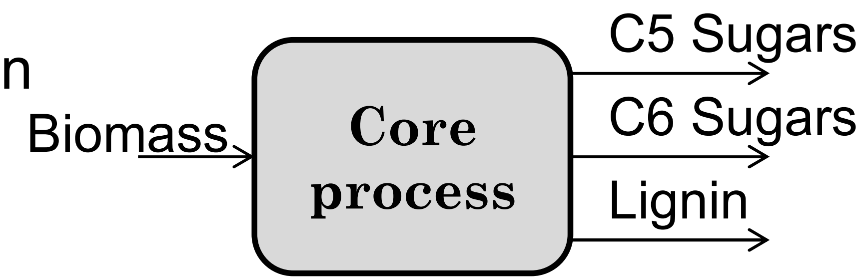
Process intensification - ISPR

- Motivation to combine reaction and separation
  - Reactions at low temperatures
  - Irreversible reactions usually inhibited by products
  - Mass transfer limitations can be important
- Exploit innovations and advances in
  - Membrane technology, materials, catalysis
- In-situ recovery is challenged by
  - Separation difficulties and an abundance of azeotropes
- Current practice
  - Industrial equipment usually very simple
  - No time to experiment for novel technologies
  - Experimentation in the lab

Illustration - IBE standalone reaction

Expand the lignocellulosic biorefinery (core process)

- **Core process:** ***Biomass*** fractionation
  - ✓ C5 Sugars (xylose)
  - ✓ C6 Sugars (*Glucose*)
  - ✓ Lignin



- *Glucose* conversion to ***IBE***
  - ✓ anaerobic fermentation

- Experimental groups ➔ conversion yields

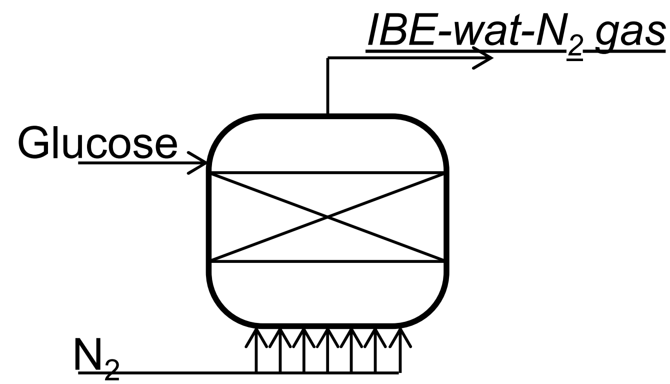
1000 kg dry biomass (wheat straw)		
390 kg Glucose		
Isopropanol	Butanol	Ethanol
39 kg	65 kg	7 kg

Illustriation – IBE: reaction and separation

Process design concept

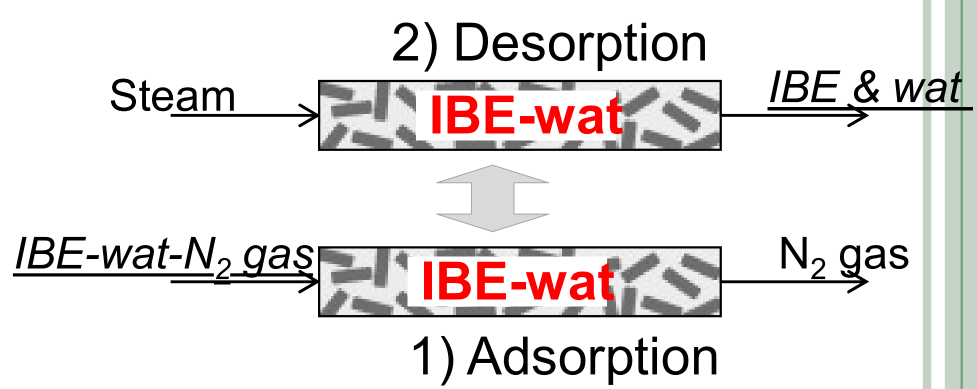
1. ***Fermentation***

- Butanol ➔ Inhibitor
- In-situ removal of alcohols ➔ N2 stripping
- 100% glucose conversion



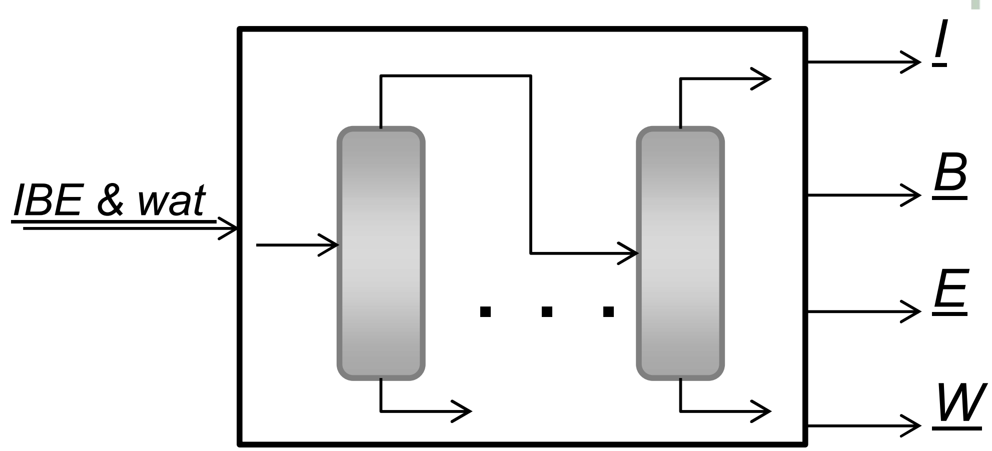
2. ***Alcohols recovery***

- Gas adsorption
- Activated carbon



3. ***Alcohols purification***

- Azeotropes & 2-phase liquids
- Distillation-Decantation system
- Complex separation
- Residue Curve Maps tool



LEVERHULME TRUST

Models - reactive separation schemes

1. *Fermentation*

- Glucose : 7300 kg/hr
- Fermentation: 53 hr ➔ 100% conversion
- Volume: 6400 m^3 ➔ 15 parallel reactors

2. *Alcohols recovery*

- Selectivity: **B**utanol > **I**sopropanol > **W**ater > **E**thanol
  1. ***B + I + W + E***
  2. ***B + I***
  3. ***B***

Process scenarios

? Profitability / ? CAPEX / ? OPEX

Scenarios		Adsorber capacity
1	B + I + W + E	11250 tn
2	B + I	390 tn
3	B	90 tn

- **Adsorption mathematical modeling**
  - √ Kinetics estimation
  - √ Minimize adsorber capacities

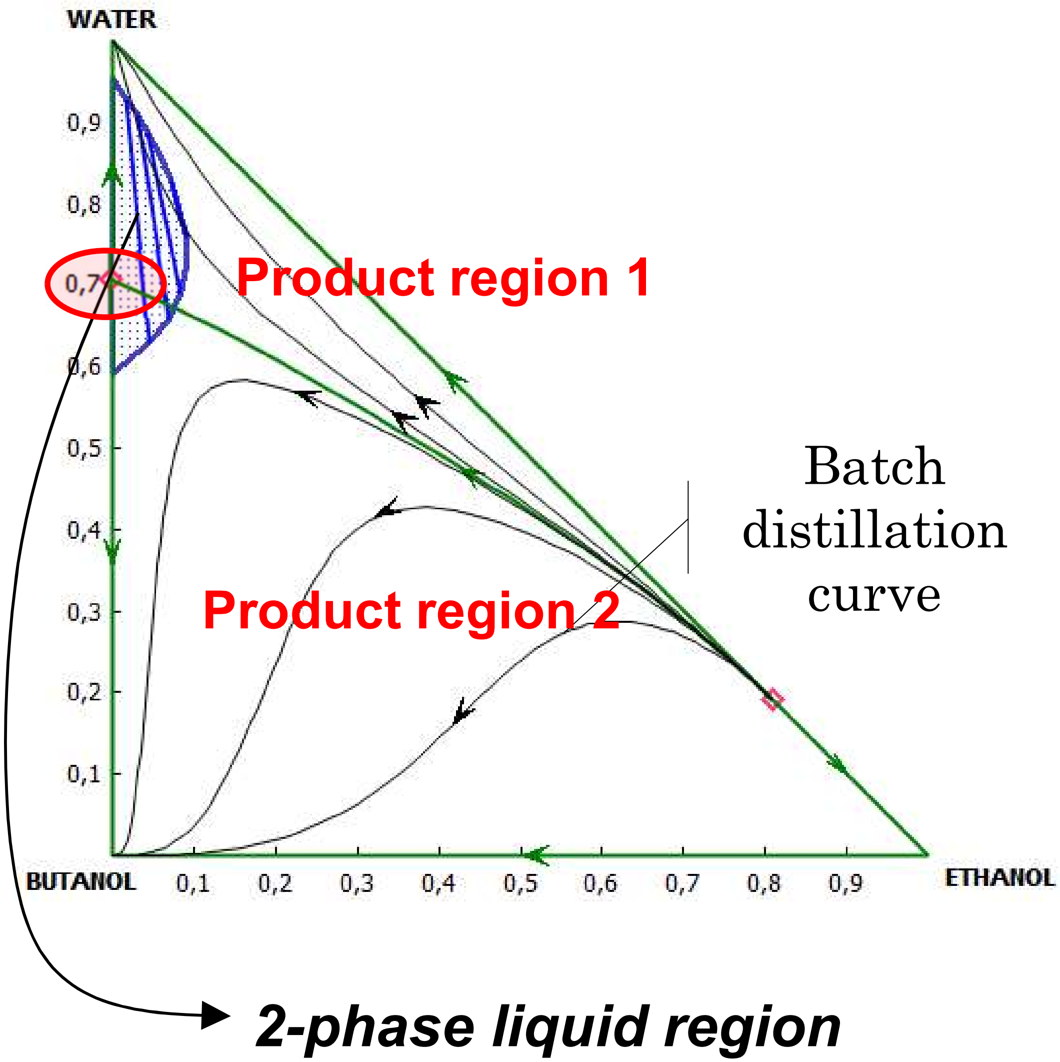
- **Desorption mathematical modeling**
  - √ Kinetics estimation
  - √ Desorption heating needs

Scenarios		Heating [MW]	Cooling [MW]
1	B + I + W + E	193	190
2	B + I	11.5	11.0
3	B	4	3.8

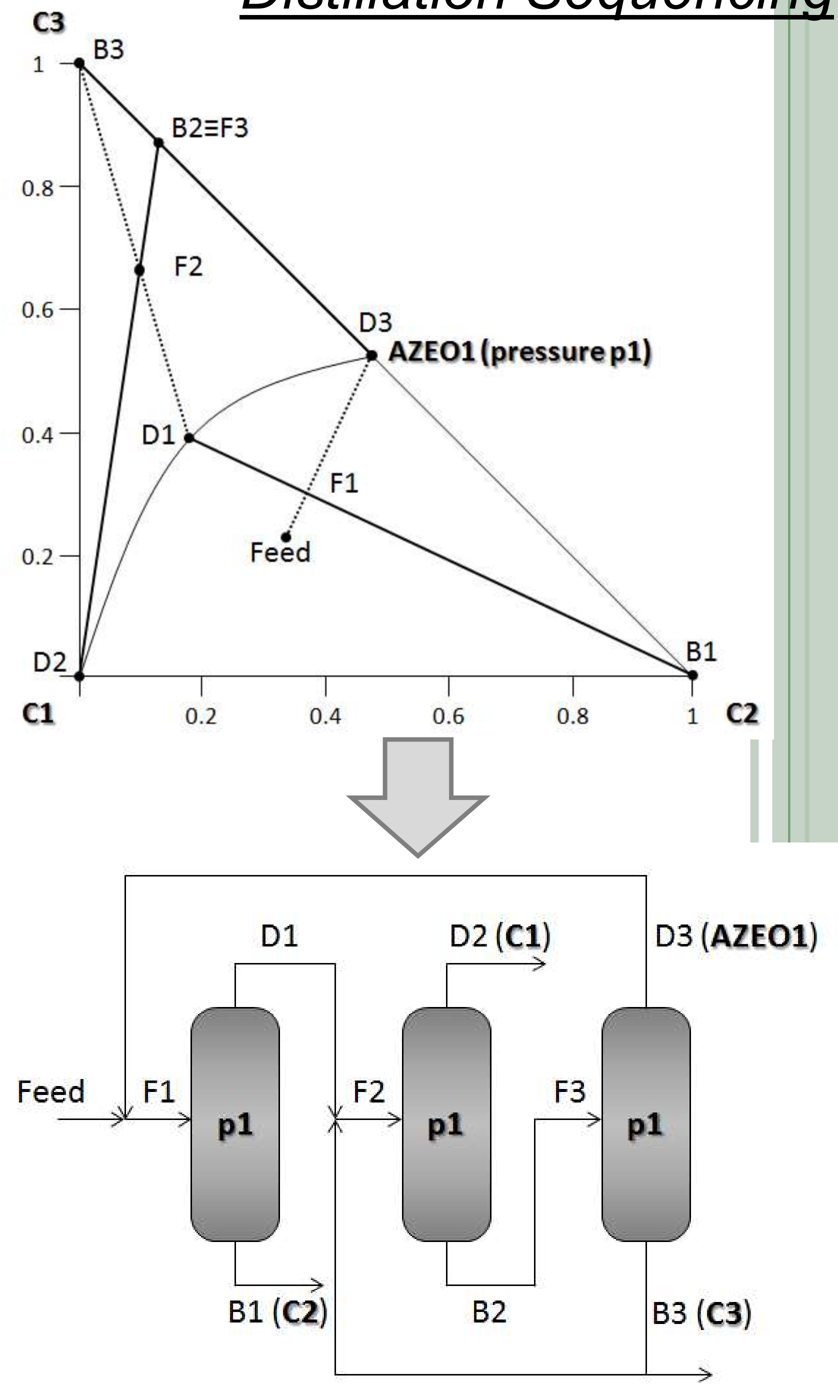
Capture knowledge of phase equilibria

3. *Alcohols purification*

Residues Curves Map



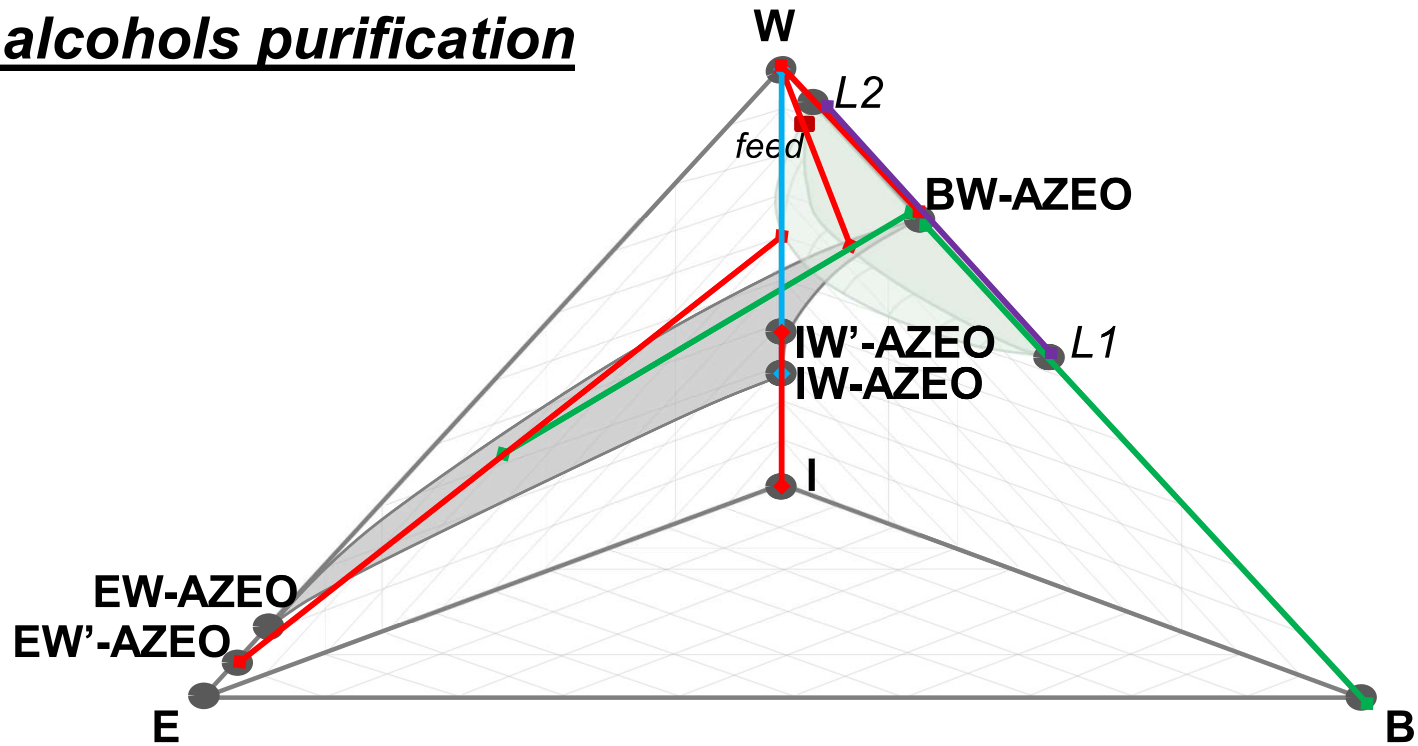
Distillation Sequencing

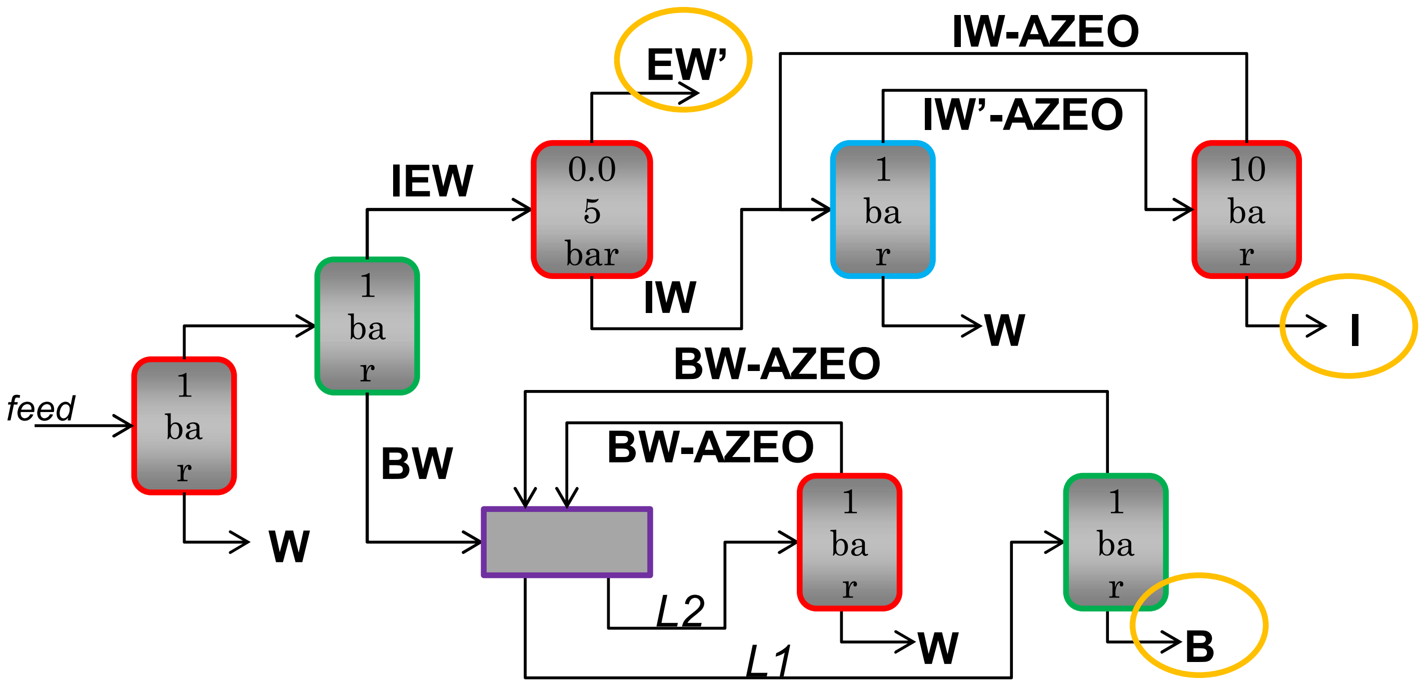


LEVERHULME TRUST

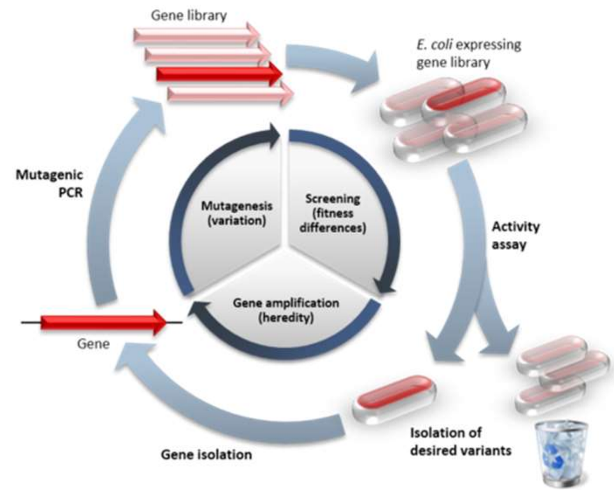
Advanced models and optimization

3. *IBE alcohols purification*

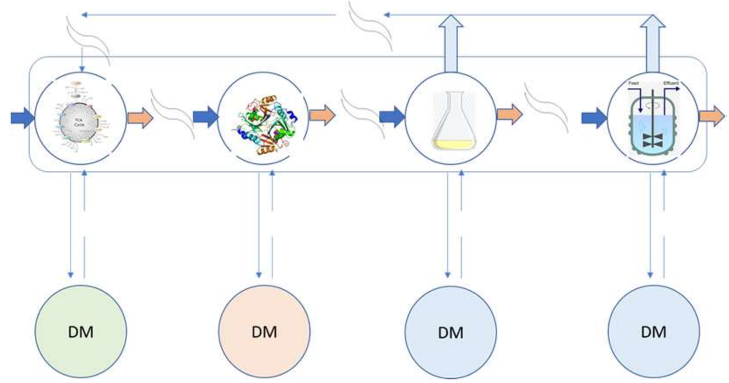




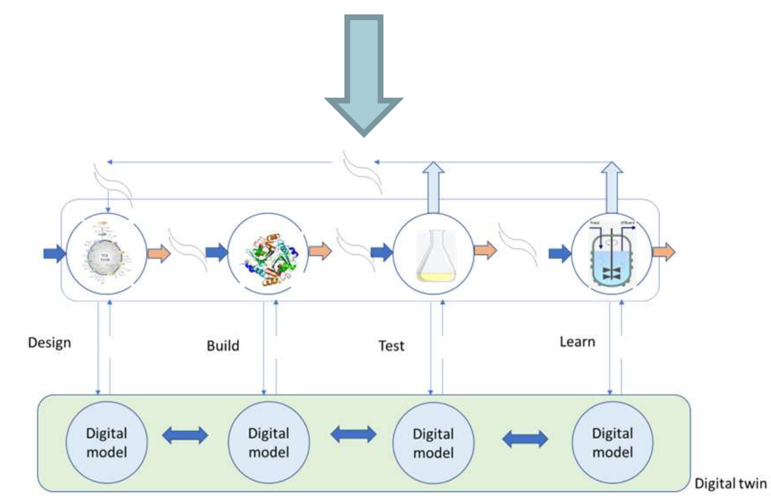
DIGITAL TWINS AND PROCESS INTELLIGENCE (INDUSTRIAL BIOTECHNOLOGY APPLICATIONS)



- Integrates development stages of different, often weakly associated, first principles.
  - **Digital twins**, equation-free representations to systematically combine knowledge domains of different (e.g. technical allopoietic & autopoietic biological systems)

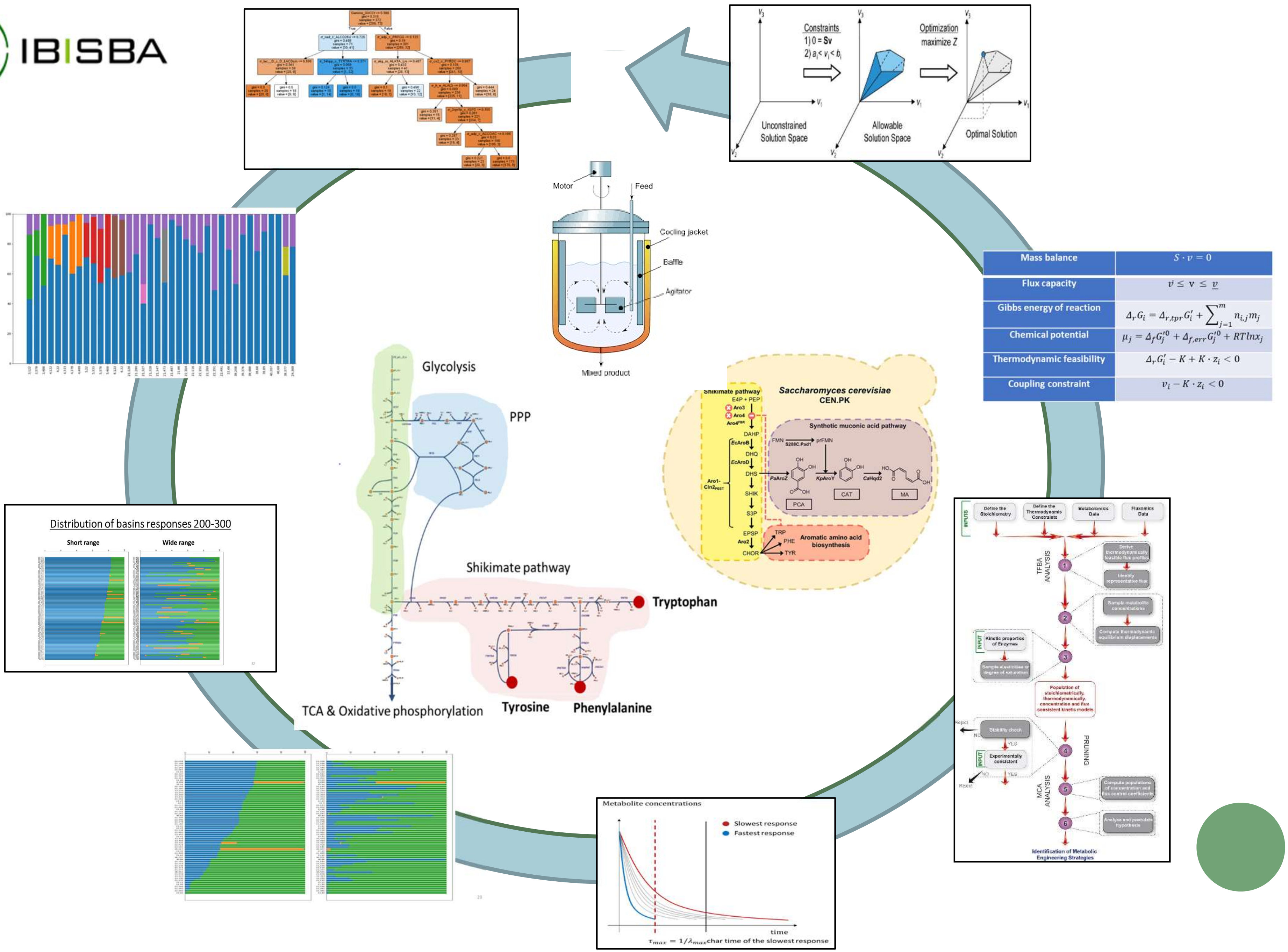


- High-throughput environment. Connect early development stages with final stages and validation
  - **Digital twins** by means of deep learning methods and decision trees guide process and product design decisions.
- Manufacturing intelligence translates into a systematic integration of knowledge and expertise enabling to reverse-engineering decision flows.
  - **Digital twins** could be natural to invert input-output structures for control purposes and reverse links with cell engineering.



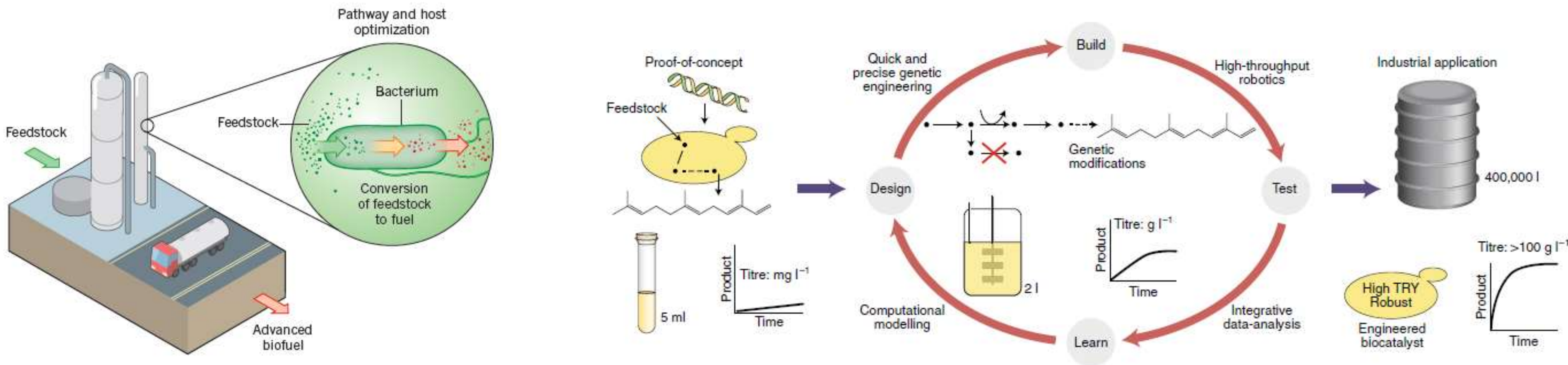
IBISBA

Connect Curated kinetics with real-life



Mass balance	$S \cdot v = 0$
Flux capacity	$\bar{v} \le v \le \underline{v}$
Gibbs energy of reaction	$\Delta_r G_i' = \Delta_{r,tpr} G_i' + \sum_{j=1}^{m} n_{i,j} m_j$
Chemical potential	$\mu_j = \Delta_f G_j'^0 + \Delta_{f,err} G_j'^0 + RT \ln x_j$
Thermodynamic feasibility	$\Delta_r G_i' - K + K \cdot z_i < 0$
Coupling constraint	$v_i - K \cdot z_i < 0$

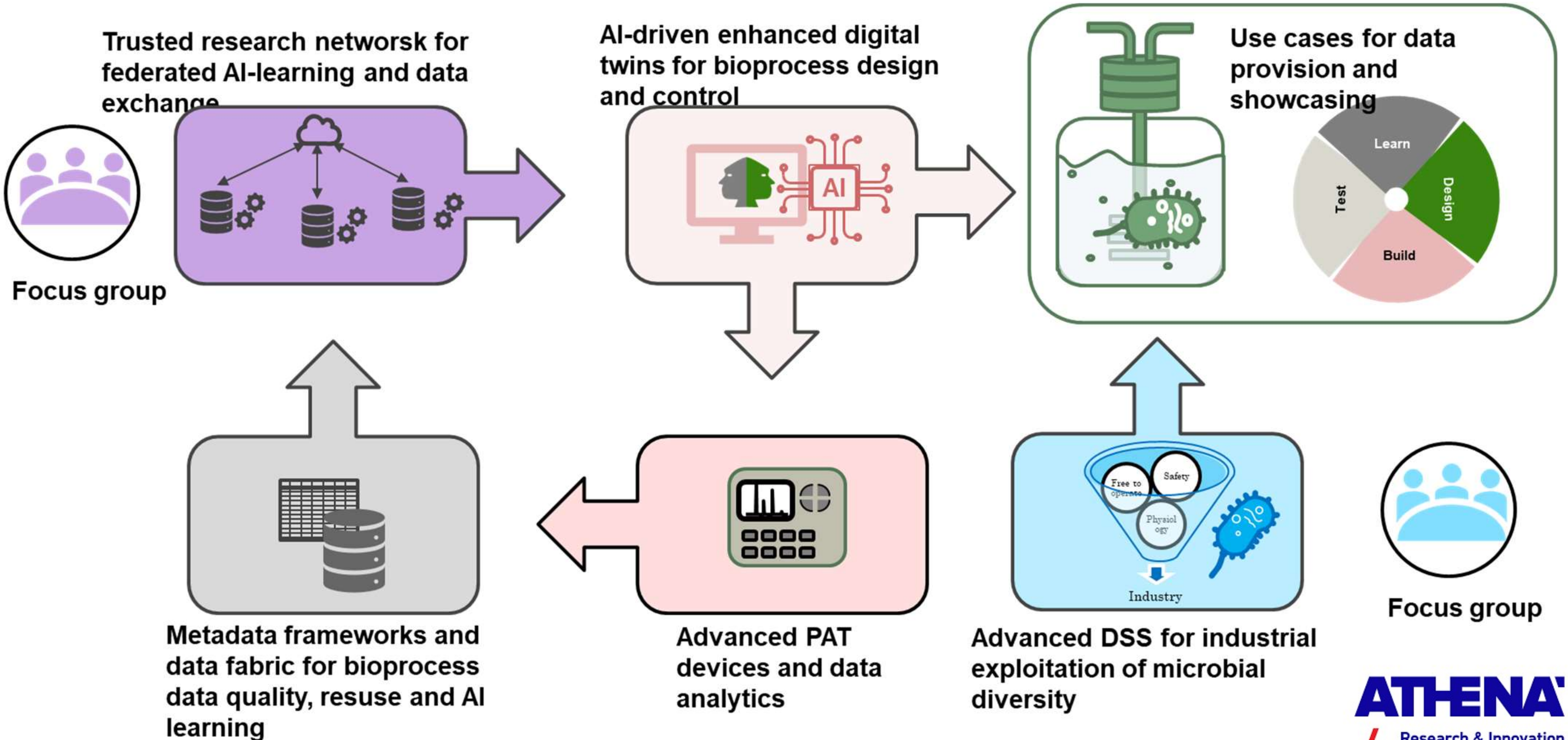
Design-Build-Test-Learn cycle for process and strain design



- Current Computational modeling approaches employ Genome-Scale Metabolic models (GSMs) to identify network adjustments that lead to maximum Yields
- Most common approaches include MILP formulations suggesting Gene Knock-outs, upregulations and downregulations
- While the downstream cost plays a decisive role in a future process sustainability, the existing metabolic engineering approaches do not take it into consideration

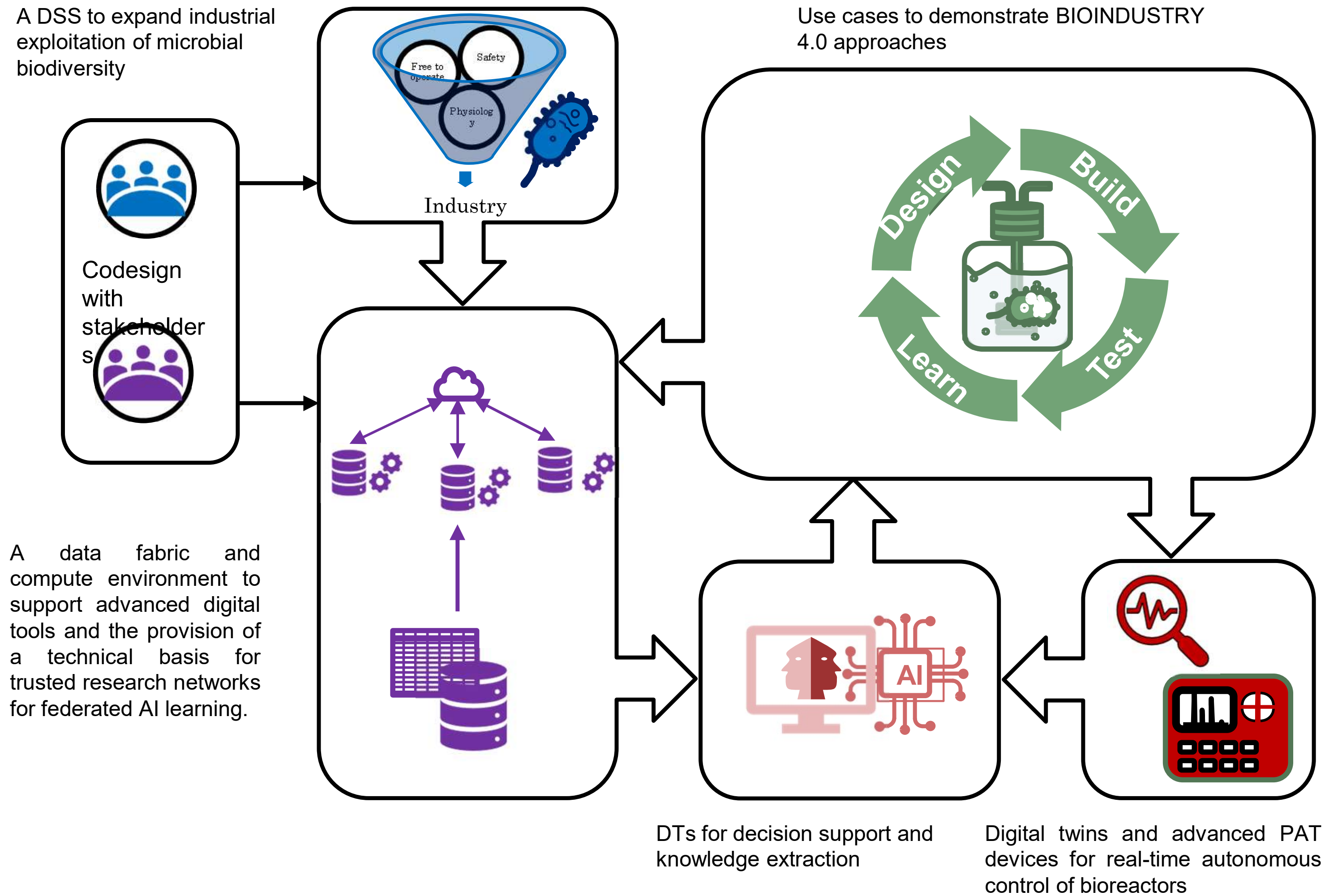
IBISBA

Digital twinning – industrial reactors



- Combined knowledge from online experiments, offline experiments
- Omics, GSM models, curated kinetics
- Physical models of different types of reactors

DIGITAL TWINNING AS A SERVICE

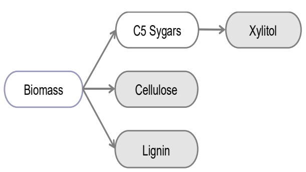


DT as a service to industry and the community

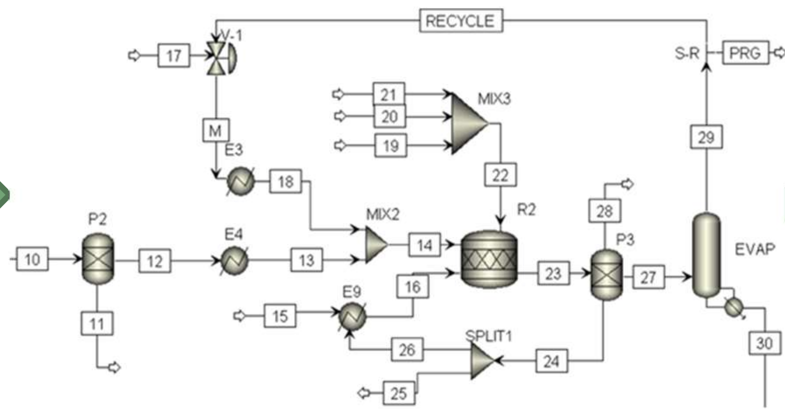
Ex-ante analysis – ex-ante LCA

State-of-practice (ex-post)

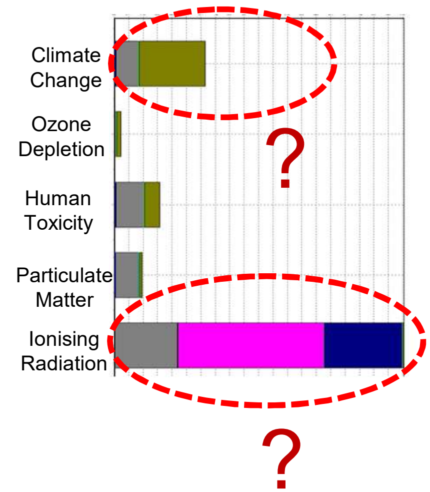
Background system



Foreground system



LCA performance

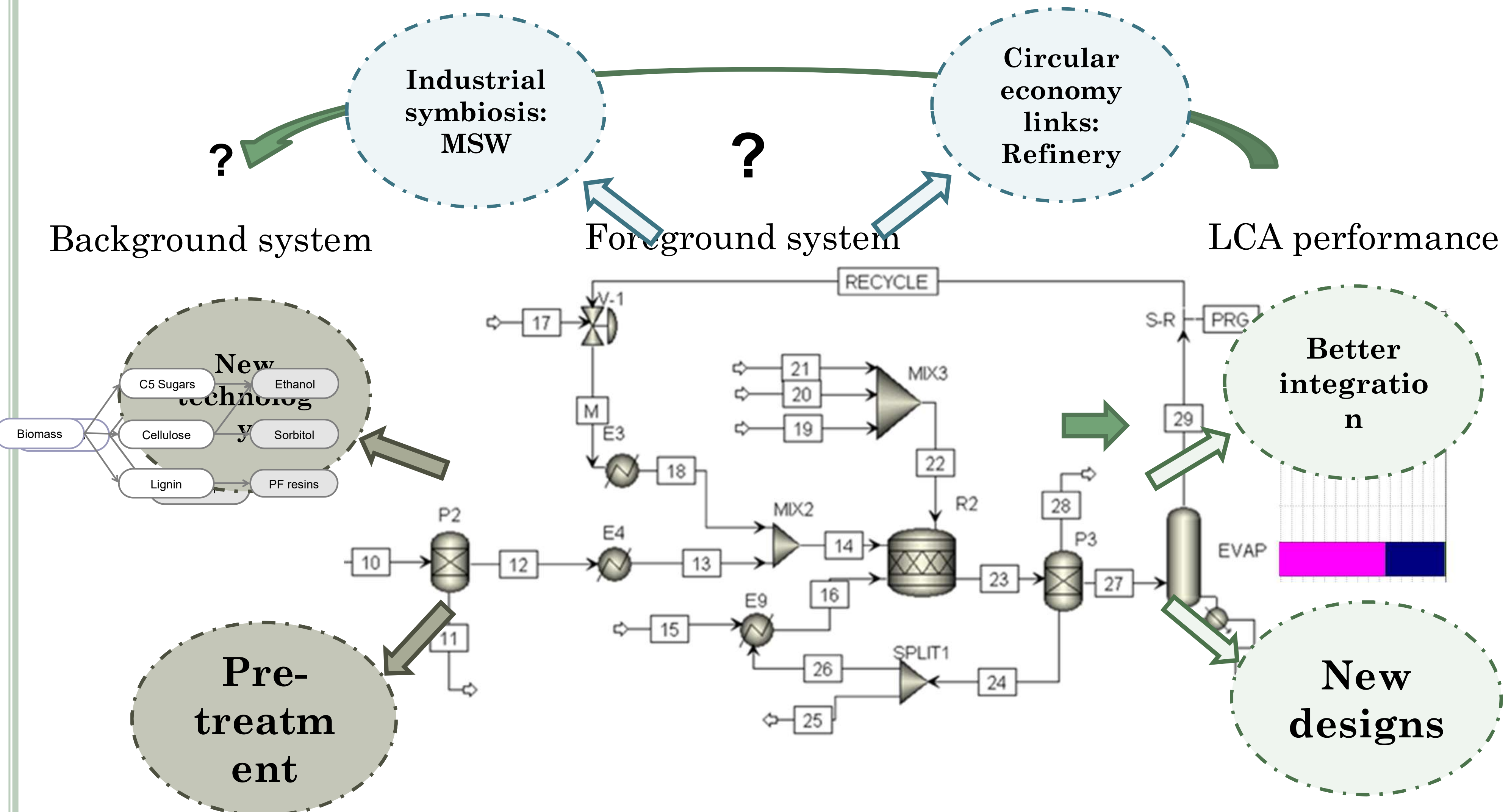


End of line (forward) evaluation

- Inventories through foreground simulations and optimization
- LCA technology

– useful to assess preliminary concept and design
– inconclusive to design decisions
– unable to connect evaluation with foreground or background

FROM EX-POST EVALUATION…



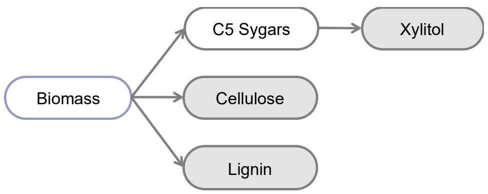
… to reverse-engineering and decision-making

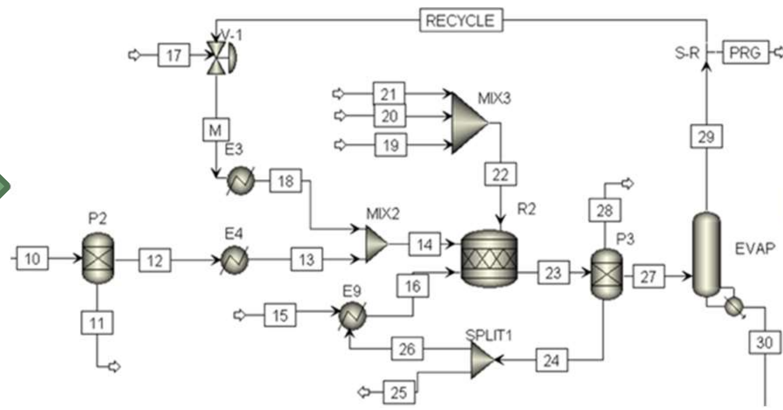
LCA and the challenge of data

Background system

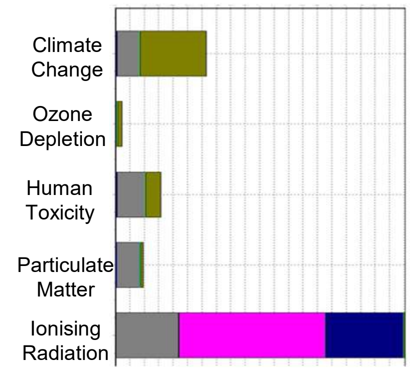
Foreground system

LCA performance



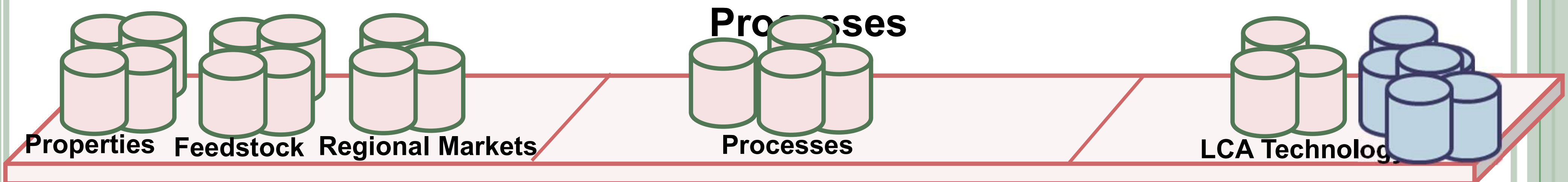


Chemicals



Background **Foreground** **LCA**

Processes



Background **Foreground** **LCA**

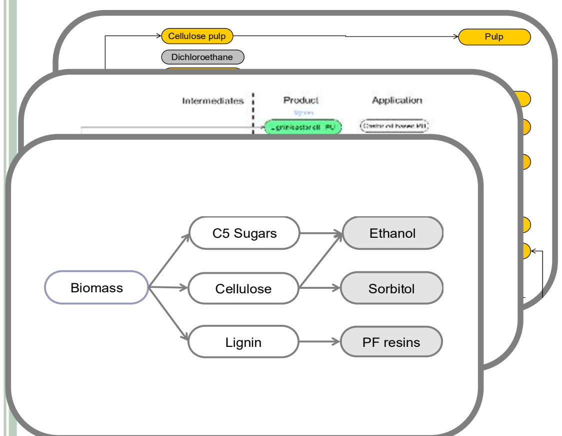
Data challenges and machine learning

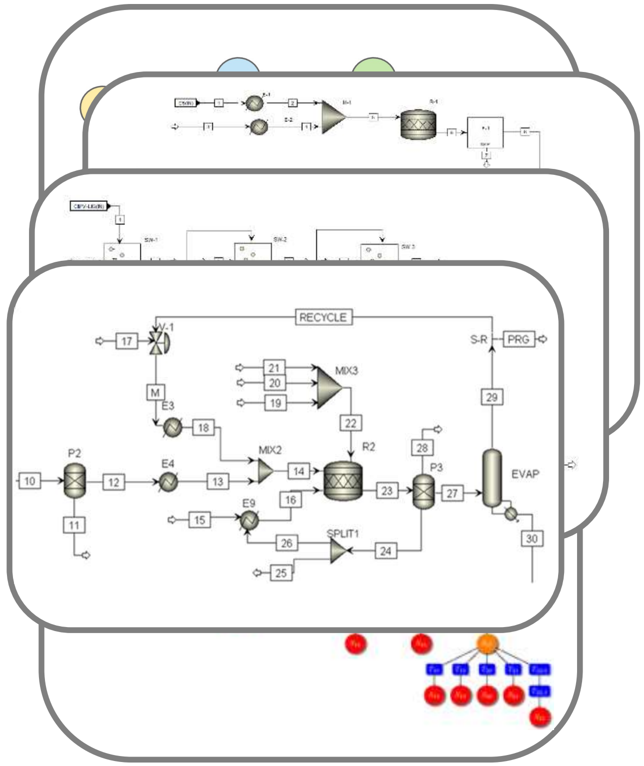
- Basic idea: use background context and foreground inventories to train LCA models for selected industries

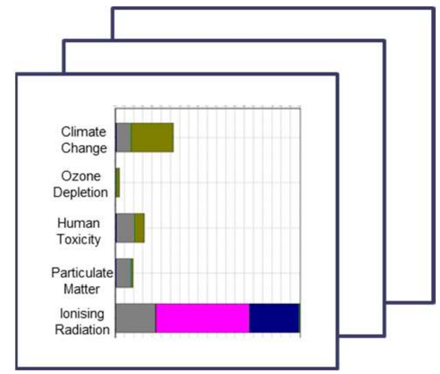
Background system

Foreground system

LCA performance







Input

Output

Use machine learning to produce inventory-free LCA

INPUT-OUTPUT STRUCTURE

Background set

- 35 candidates: 26 available in lab scale (reduced set models), 9 available in conceptual level process design (detailed set of models)

1. Synthesis path
   - Biomass conversion *(e.g. chemical, biochemical, thermochemical)*
   - Mass intensity *(reactants, solvents, catalysts, etc. used in synthesis path)*
   - Co-production *(co-products per path), m*umber of processing steps
2. Process related
   - Maximum reaction temperature (lab scale)
   - Number of endothermic/exorthermic reactions per path (lab scale)
3. Product related
   - Molecular weight, functional groups,
   - number of oxygen/carbon/H2 atoms, carbon/H/O ratio

Choices for foreground variables

A wide range of biorefinery flowsheets spanning across

- 1st generation inventories
  - Biodiesel (bio-esters), bioethanol, biogas
  - Produced from food biomass (sugars, starch)
  - Mature technologies
- 2nd generation inventories
  - Lignocellulosic sources, oleochemical, algae
  - Varieties of fractionation technologies
- 3rd generation inventories
  - Algae, biogenic waste
- Inventories assume
  - Different levels of integration
  - No account of circular economy or industrial symbiosis

LCI DATA SETS

Mid-point impact categories (RECIPE method)

1. Climate change **(CC)**
2. Ozone depletion **(OD)**
3. Human toxicity (HT)
4. Photochemical oxidant formation **(POF)**
5. Particulate matter formation **(PMF)**
6. Terrestrial acidification **(TA)**
7. Ionising radiation **(IR)**
8. Eutrophication Fresh Water **(FE)**
9. Eutrophication marine **(ME)**
10. Terrestrial ecotoxitciy **(TE)**
11. Fresh water ecotoxitciy **(FET)**
12. Marine ecotoxitciy **(MET)**
13. Land occupation (Agricultural, **(ALO)**
14. Land occupation urban **(ULO)**
15. Natural land transformation **(NLT)**
16. Metal depletion **(MD)**
17. Fossil depletion **(FD)**
18. Water depletion **(WD)**

End-point damage categories (RECIPE method)

19. Ecosystems quality **(EQ)**
20. Resource depletion **(RD)**
21. Impacts to Human Health **(HH)**

Total score metrics

22. Total RECIPE Score
23. Non renewable, fossil energy demand (CED)

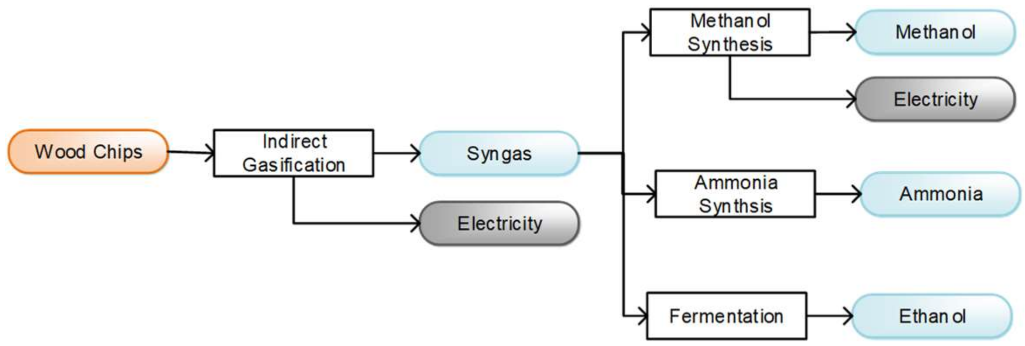
138 datasets for model development

- 23 LCA metrics
- 3 allocation methods
- 2 sets of independent variables (full/reduced):
  - 35 input variables
  - 26 independent variables

Machine learning technology:
- Decision trees
- Data models

Example: selection of products

- *Problem case*
  - Need to develop product portfolio from wood-chips
  - Value chain includes intermediates and end-of-line products that involve methanol, ammonia and ethanol
  - Use Climate Change (CC) and Cumulative Energy Demand (CED) for environmental assessment



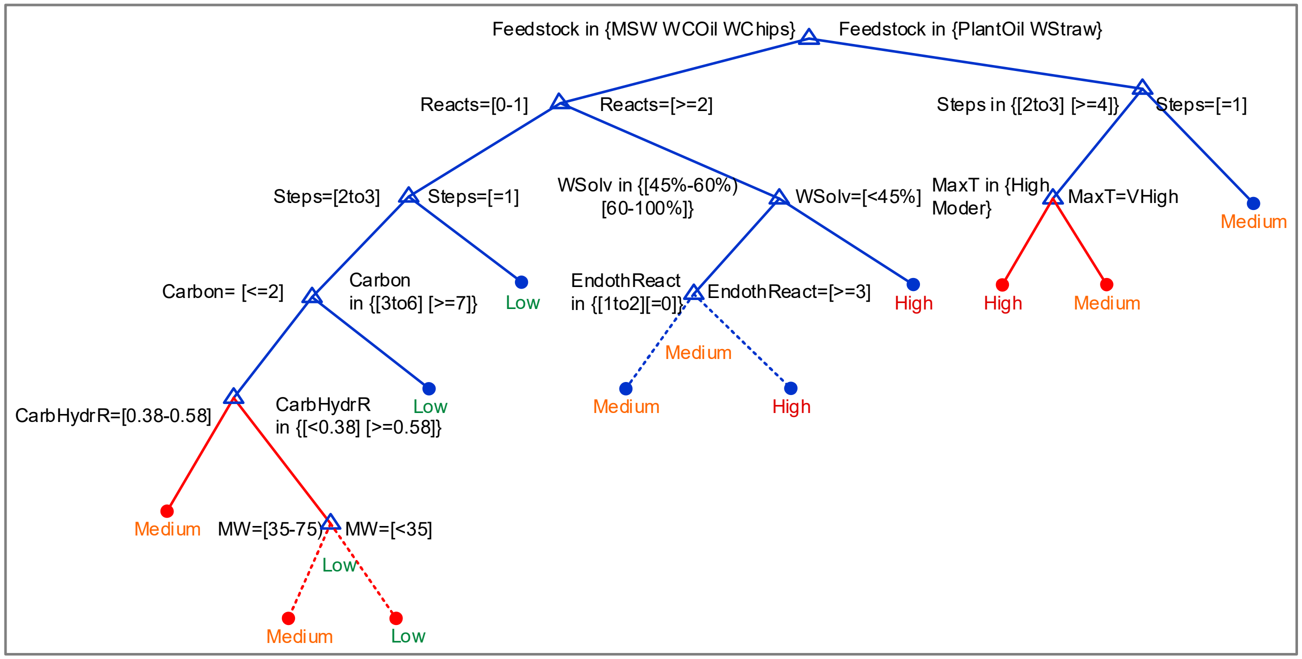
- *Objective: Inventory-free*
  - Assessment of options ahead of inventory calculations
  - Ranking relevant merits between choices

Ex-ante approach

Identify paths:
Biomass→ Methanol (1)
Biomass → Ammonia (2)
Biomass → Ethanol (3)
Also,
Combinations of the above

Data required

	Methanol (1)	Ammonia (2)	Ethanol (3)
Feedstock	*WChips*	*WChips*	*WChips*
Reacts	0	0	0
Steps	2	2	2
Carbon	*(<=2)*	*(<=2)*	*(<=2)*
CarbHydrR	*<0.38*	*<0.38*	*<0.38*
MW	*<35*	*<35*	*35-75*



Decision tree for Climate Change

EX-ANTE VS CONVENTIONAL LCA

CED evaluation: ex-ante LCA model vs inventory-based approach

	Estimation	Real class	Value	
Methanol	Low	Low	5.87	√
Ammonia	Low	Low	2.14	√
Ethanol	Medium	Medium	13.3	√

- ✓ Correct ranking
- ✓ Correct class estimations

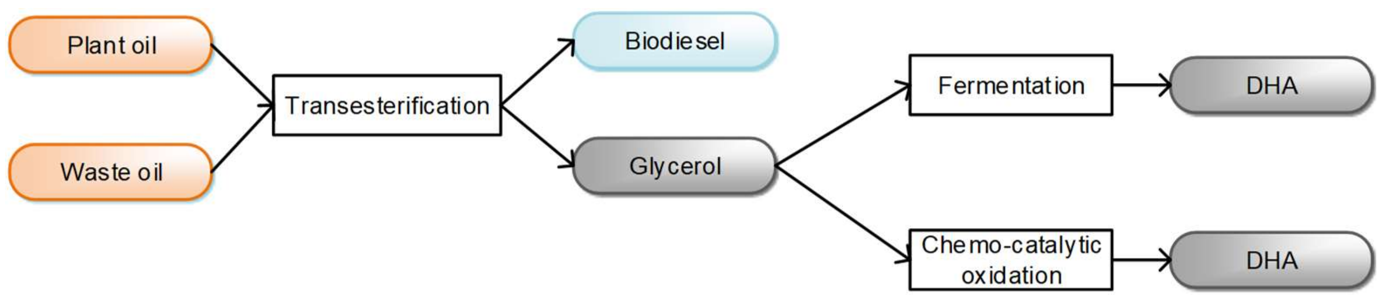
CC evaluation: ex-ante LCA model vs inventory-based approach

	Estimation	Real class	Value	
Methanol	Low	Low	Low	√
Ammonia	Medium	High	Medium	X
Ethanol	Low	Low	Low	√

- ✓ Correct ranking
- ✓ One wrong class estimation

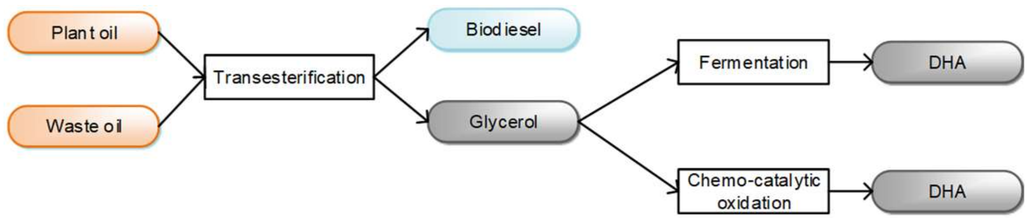
Example: selection of technologies

- *Problem case*
  - Production of di-hydroxy-acetone
  - Combination of biochemical and chemo-catalytic methods
  - Climate Change (CC) as environmental metric



- *Objective: Inventory-free*
  - Selection of technologies and feedstocks
  - Assessment of options for feedstocks: waste cooking oil, plant oil

Ex-ante approach(es): trees and ANNs



Decision trees: 4 candidate options

1) Plant oil→ Glycerine -->Biochemical process→DHA
2) Waste cooking oil -> Glycerine --> Biochemical process →DHA
3) Plant oil → Glycerine -->Chemocatalytic process→DHA
4) Waste cooking oil → Glycerine --> Chemocatalytic process →DHA

EX-ANTE: DECISION TREES

CC evaluation: decision trees vs inventory-based approach

Case study	Rules sequense	Estimation	Real class	Value	
1 (Biochemical, Plant oil)	Feedstcock (plant oil)→Steps (=2)→ MaxT (Moder)→ Oxygen(=1)	Medium	High	9.4	(Morales, et al., 2015; Zhang, et al., 2003)
2 (Biochemical, Waste Cooking oil)	Feedstcock (WCoil)→ Reacts(=1)→ RME(=Medium)→WAirReacts(50%)	Low	High	6.4	(Morales, et al., 2015; Zhang, et al., 2003)
3 (Chemical, Plant oil)	Feedstcock (plant oil)→Steps (=2)→ MaxT (High)→ Oxygen(=1)	Medium	High	5.3	(Lari, et al., 2016; Zhang, et al., 2003)
4 (Chemical, Waste cooking oil)	Feedstcock (WCoil)→ Reacts(=1)→ RME(=Low)→ WRO(=Low)	Low	Medium	1.8	(Lari, et al., 2016; Zhang, et al., 2003)

Ex-ante ranking starting from least favorable (2&4), (1&3)
Inventory-based ranking (4), (1, 2, 3)

- ✓ *Identification of the most profitable solution*
- ✓ Clear trends due to feedstock change for the same technology (1)>(2) & (3)>(4)
- X 2 class underestimations by one level
- X 1 class underestimations by one level 2

Ex-ante: ANNs

CC evaluation: ANNs model vs inventory-based approach

			30 predictor variables	24 predictor variables	18 predictor variables
		Real value	Estimation of NN (actual value)	Estimation of NN (actual value)	Estimation of NN (actual value)
1	DHA crude (biocatalytic), plant oil	9.4	6.28	4.84	5.72
2	DHA crude (biocatalytic), waste cooking oil	6.40	3.44	3.02	3.61
3	DHA crude (chemocatalytic, oxidation), plant oil	5.3	4.35	3.82	3.51
4	DHA crude (chemocatalytic, oxidation), waste cooking oil	1.8	1.51	1.58	0.99

✓ *Identification of the most profitable solution*

X High deviations from actual values

- ANNs match closely inventory-based results (1)>(2) & (3)>(4)
- In 18 predictor variables they succeed 100% in the reported solutions

CONCLUDING REMARKS

- Experience on emerging installations
  - Sustainable production is marginal, more often it is not
  - Proper integration is prerequisite for economic sustainability
  - Significant room for innovations consider upstream technologies as well as a wider context of interactions
- Process systems engineering:
  - Instrumental to address challenges and build efficiencies
  - Necessary to assist experimental work
  - Can exploit a lot from past experience but there is also room for entirely new applications
- Biorefineries is essentially a small part of a larger problem
  - Circular economy and energy markets
  - Renewable networks and sustainable infrastructures
  - Social inclusion and benefits in valorizing waste as new feedstock

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ΗΛΕΚΤΩΡ

More tomorrow – with equations!

- A game-theoretical approach for the analysis of waste treatment and circular economy

- On the integration of process engineering and synthetic biology: large-scale kinetics and the simultaneous synthesis of biocatalysts and process engineering

- On the Acceleration of Outer-Approximation Methods Using Sparse Cutting Plane populations and Data Analytics

THANK YOU!