Optimal Synthesis and Planning of Sustainable Chemical Processes

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Motivation

1. Increasing need to design sustainable energy systems and supply chains

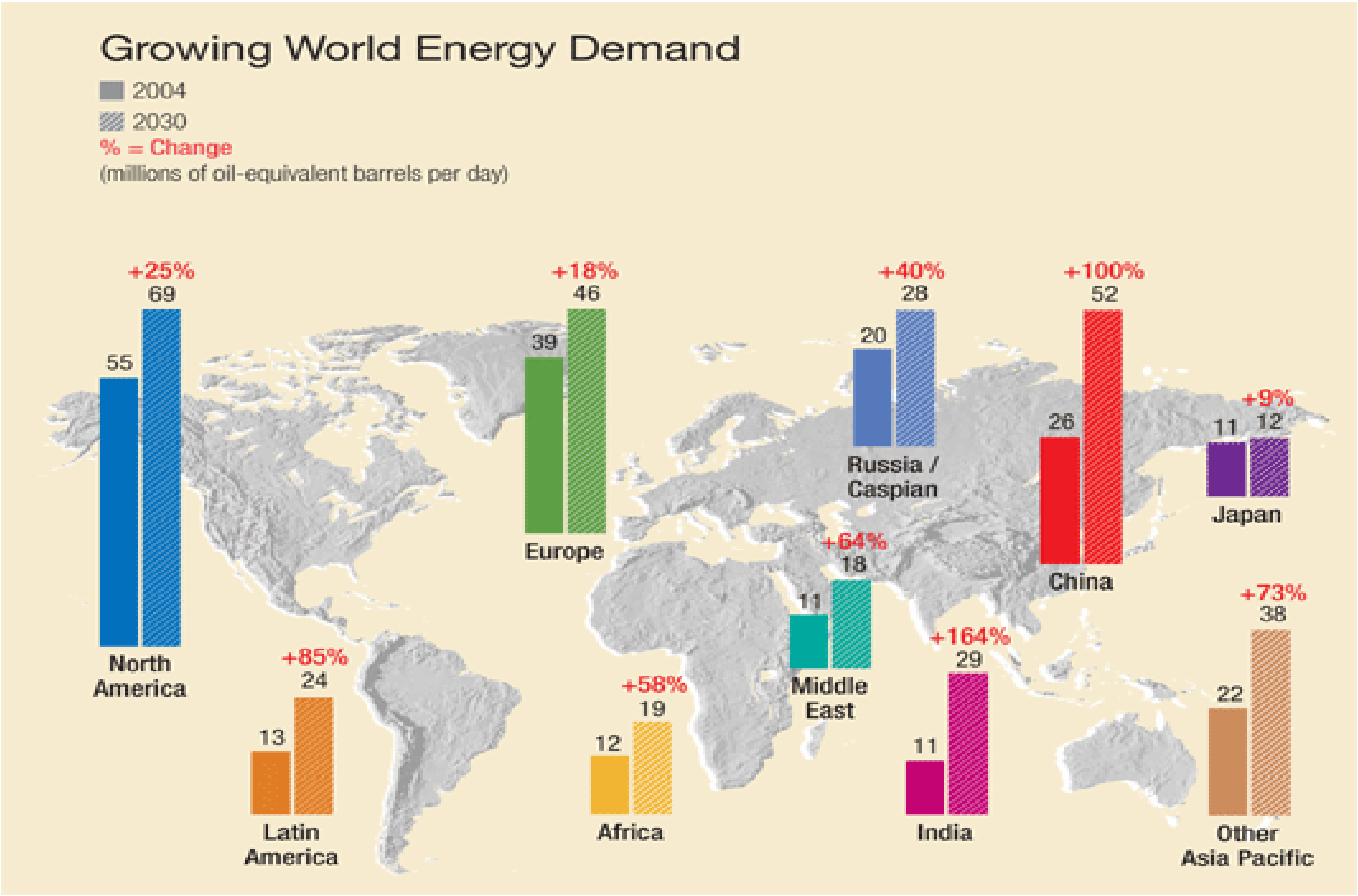
2. Need to address design of sustainable chemical processes
   - Minimize energy use
   - Minimize water consumption

3. Need to account for life cycle assessment in supply chains

Goal: Systematic Optimization Approaches for the Synthesis and Planning of Sustainable Chemical Processes

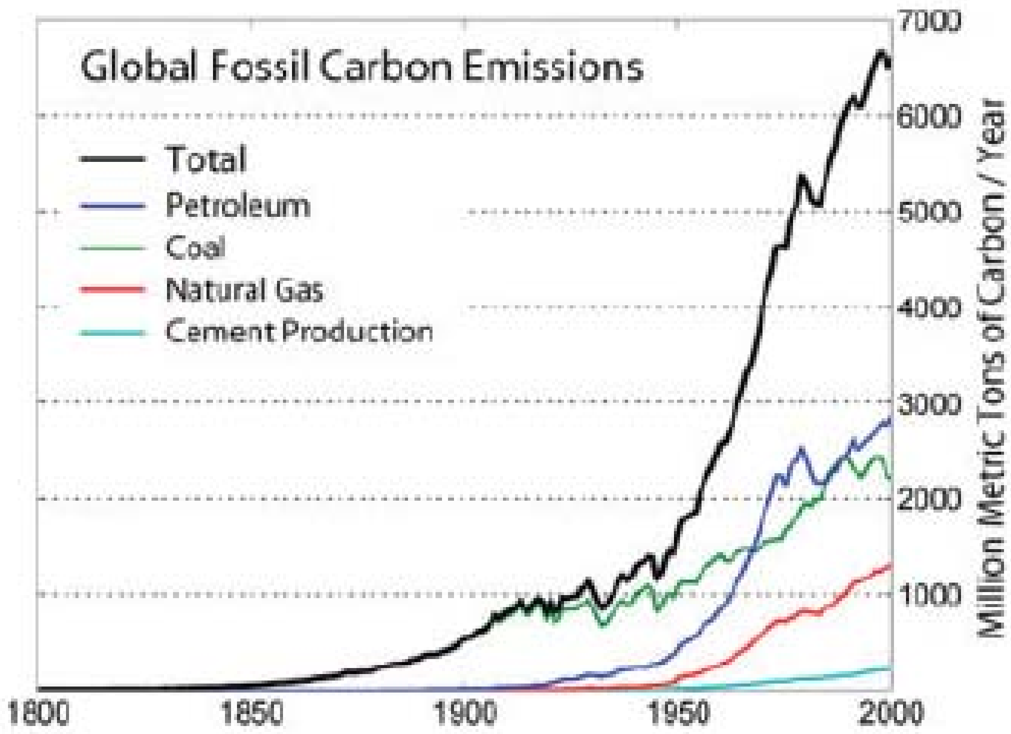
Challenges:
Develop effective mathematical programming models and solution approaches for sustainable water, energy systems, and supply chains

Energy



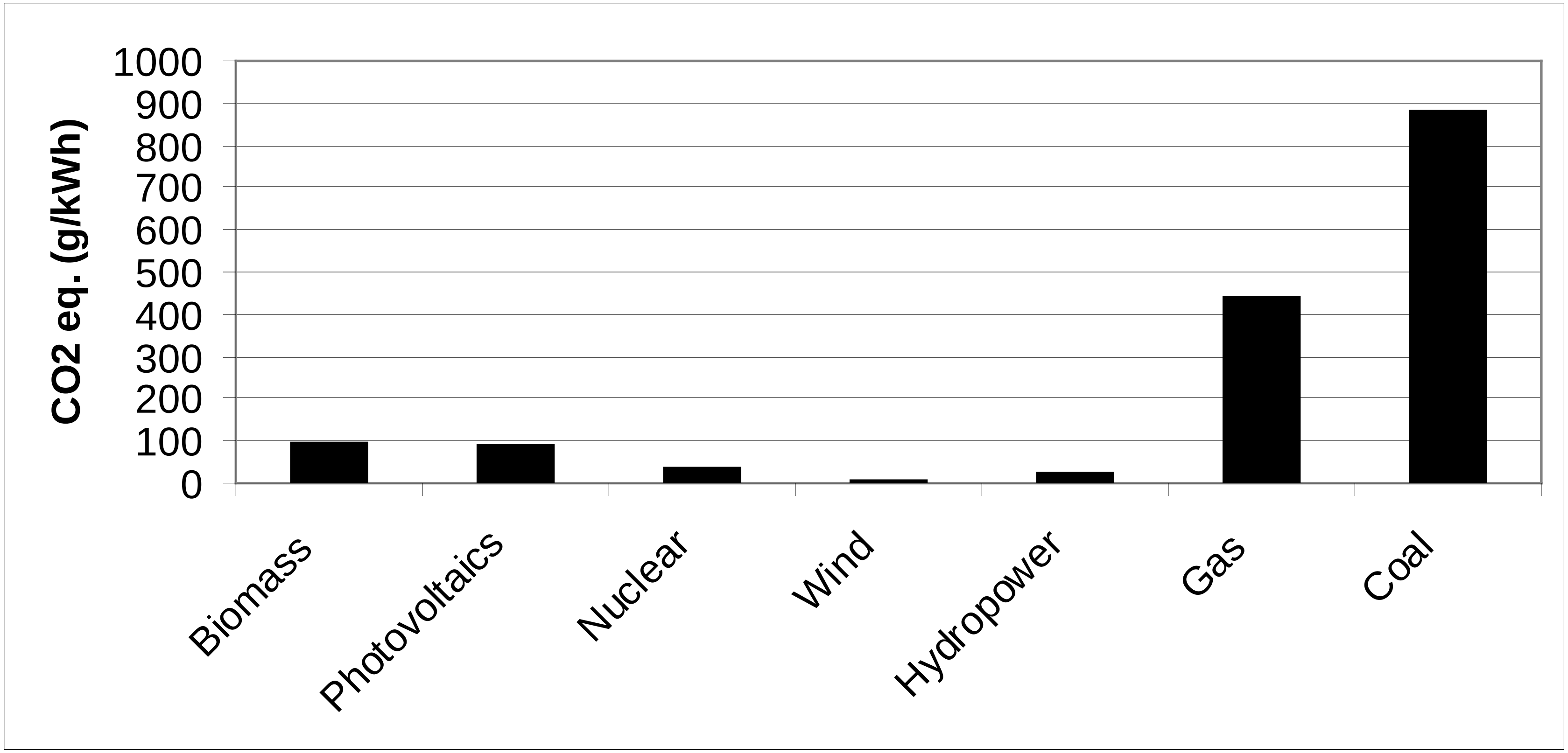
Overall 70% increase

Growing emissions of CO_2



Sheppard, Socolow (2007)

Renewables: Carbon footprint various Energy Options



Adisa Azapagic (2012)

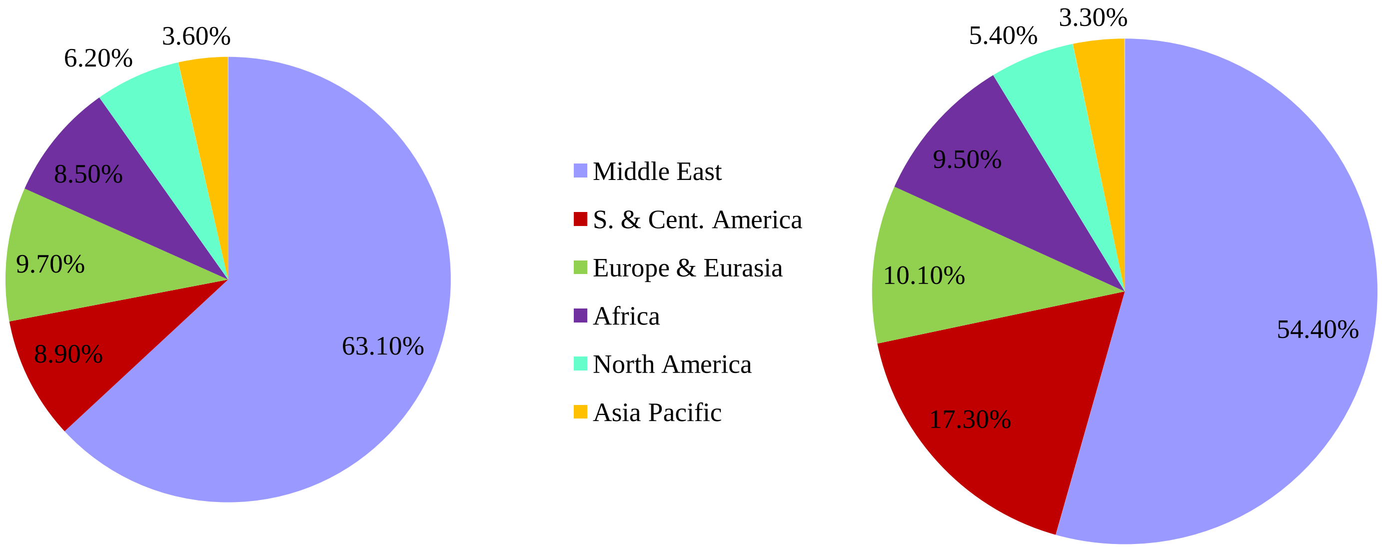
Depletion of fossil fuels?

Oil Reserves

Year 2000 — *Total: 1105 thousand million barrels*

Year 2010 — *Total: 1383 thousand million barrels*

25% increase!

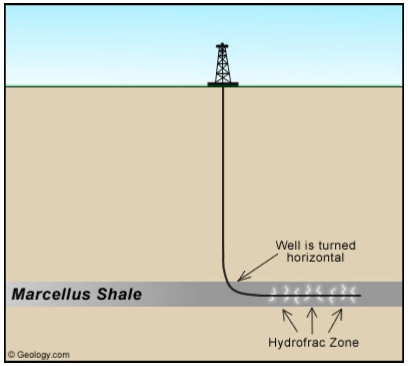


- *Discovery of New Large Oil and Gas Reserves*
- *New technologies for Offshore oil exploration and production*

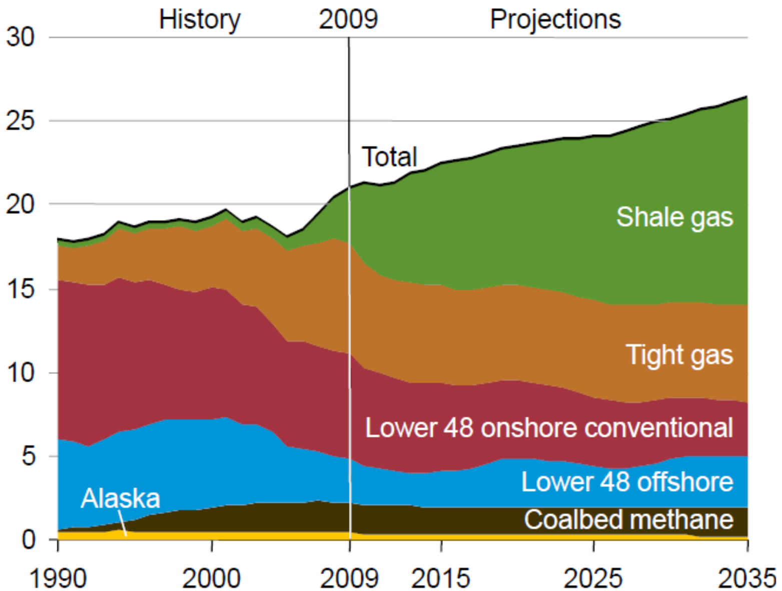
****Statistical Review of World Energy (June, 2011)***

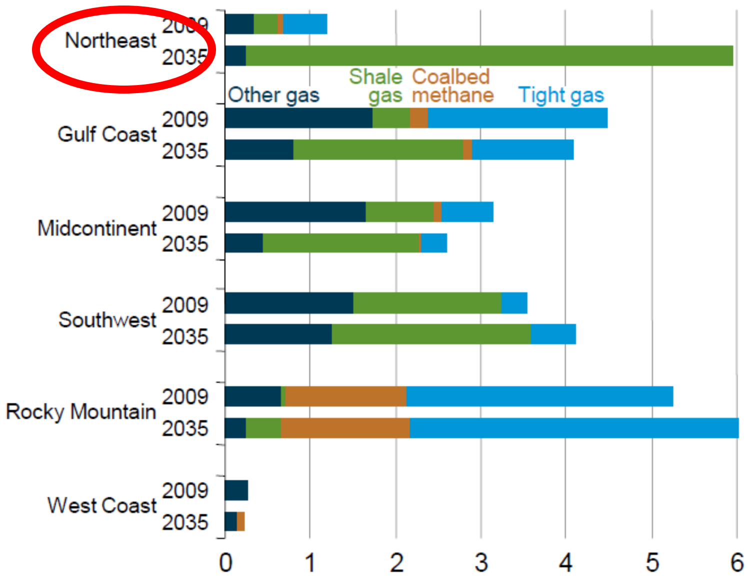
Depletion of fossil fuels?

Growth in Shale Gas



Horizontal drilling
Hydraulic fracking





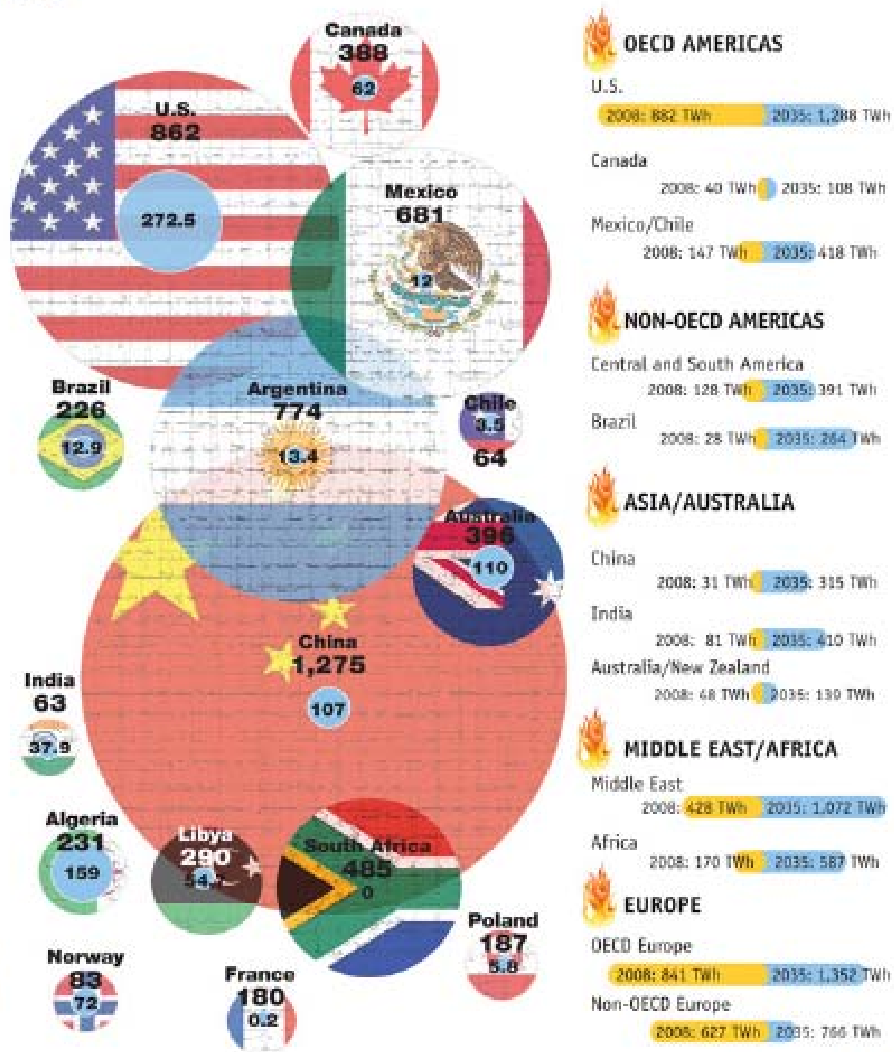
In 2035 close to 50% from Shale Gas

Northeast: from 0.3 trillion scft 2009
to 5.8 trillion scft 2035

Chemical ENGINEERING

CAPD CENTER

Shale Resources



units = trillion cubic feet

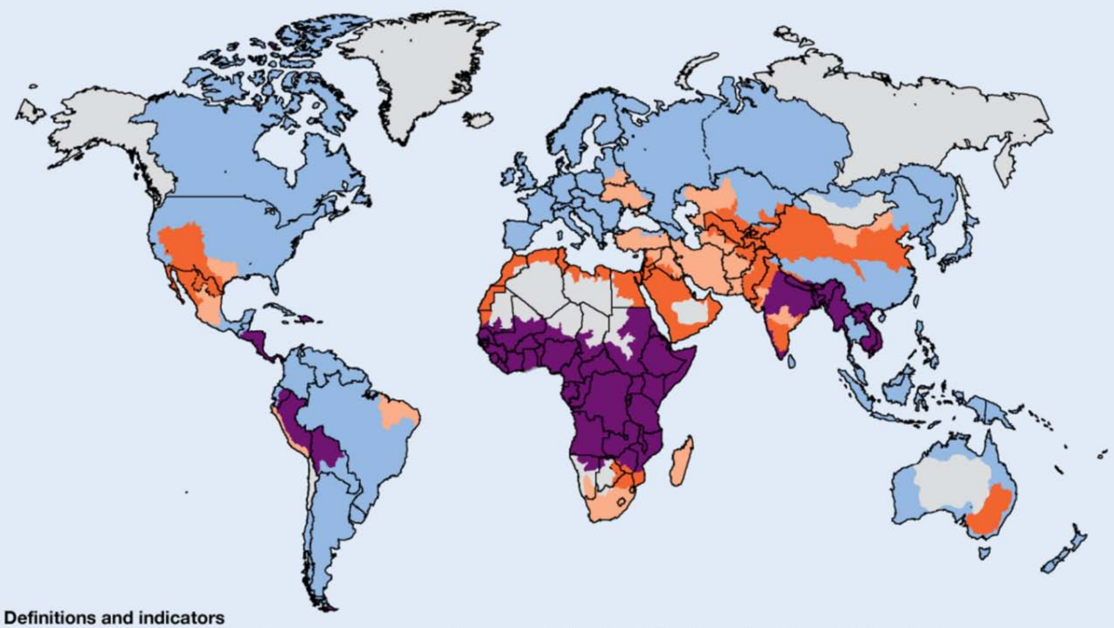
Larger circles = technical reserves
Smaller circles = potential reserves

yellow = current useage
blue = estimate for 2035

Sonal Patel, "THE BIG PICTURE: A Shale Gas Revolution", Power, June 2012

Carnegie Mellon

Water scarcity



Definitions and indicators

- *Little or no water scarcity*. Abundant water resources relative to use, with less than 25% of water from rivers withdrawn for human purposes.
- *Physical water scarcity (water resources development is approaching or has exceeded sustainable limits)*. More than 75% of river flows are withdrawn for agriculture, industry, and domestic purposes (accounting for recycling of return flows). This definition—relating water availability to water demand—implies that dry areas are not necessarily water scarce.
- *Approaching physical water scarcity.* More than 60% of river flows are withdrawn. These basins will experience physical water scarcity in the near future.
- *Economic water scarcity (human, institutional, and financial capital limit access to water even though water in nature is available locally to meet human demands)*. Water resources are abundant relative to water use, with less than 25% of water from rivers withdrawn for human purposes, but malnutrition exists.

Source: International Water Management Institute analysis done for the Comprehensive Assessment of Water Management in Agriculture using the Watersim model; chapter 2.

Two-thirds of the world population will face water stress by year 2025

Potential for Optimizing Sustainable Processes

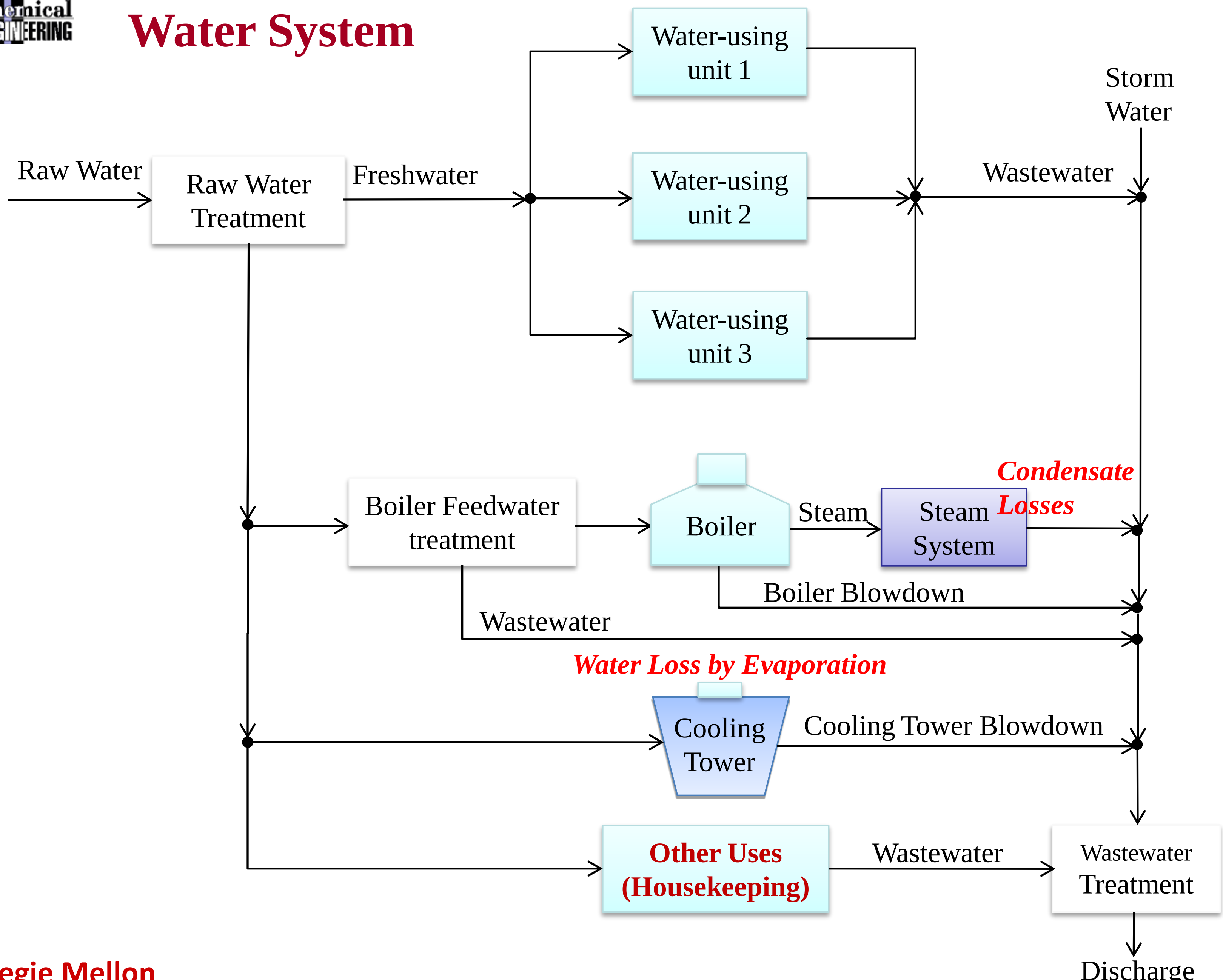
Optimal Synthesis of Water Networks and Simultaneous Optimization

Optimal Design of Biofuel Plants

Optimal Water Management for Shale Gas

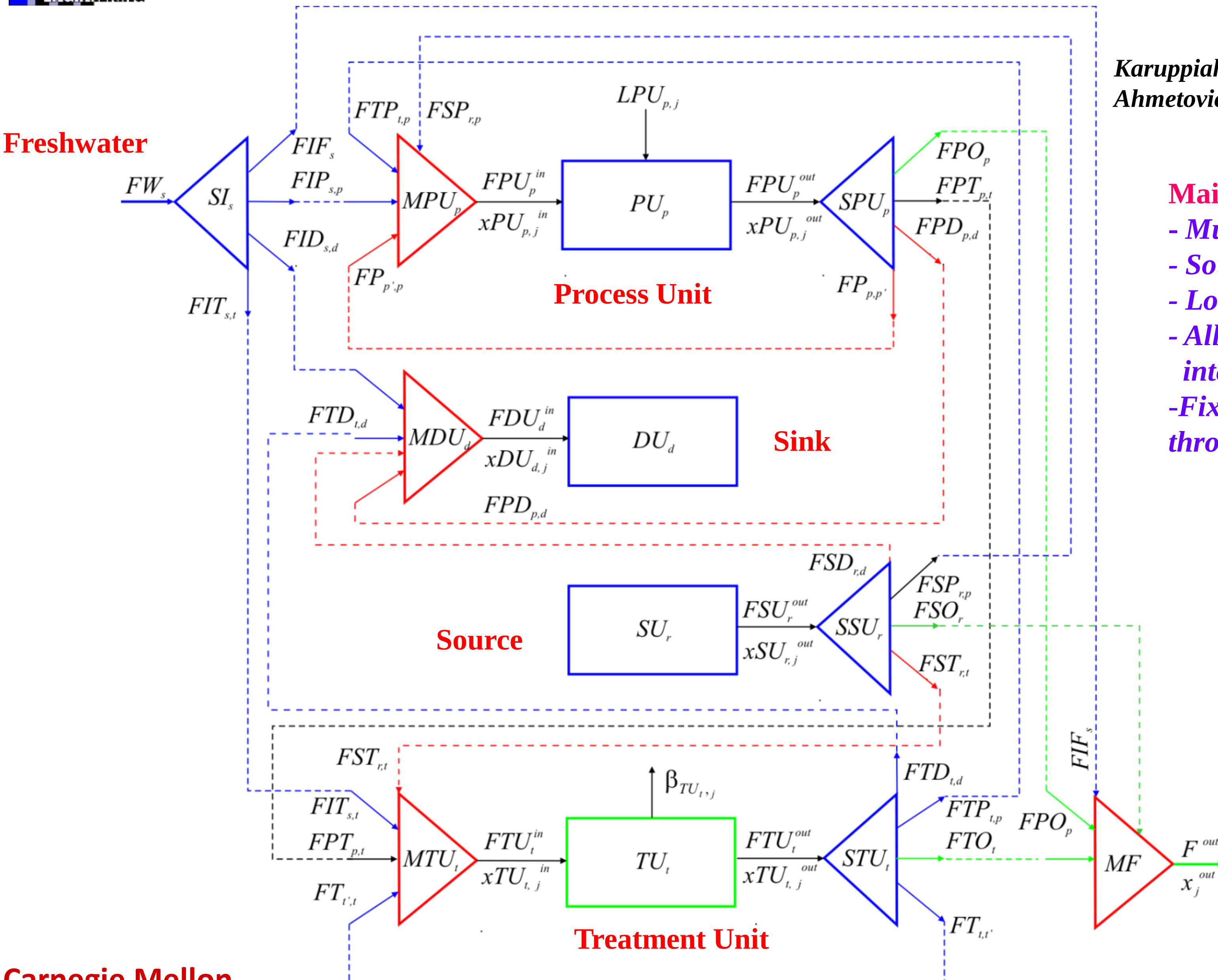
Optimal Design Energy Supply Chains

Conventional Water System



Superstructure for water networks for water reuse, recycle, treatment, and with sinks/sources water

Karuppiah, Grossmann (2008)
Ahmetovic, Grossmann (2010)



Main features:
- *Multiple feeds*
- *Source/Sink units*
- *Local recycles*
- *All possible interconnections*
- *Fixed and variable flows through process units*

Optimization Model

Nonconvex NLP or MINLP

Objective function: ***min Cost***

Subject to:

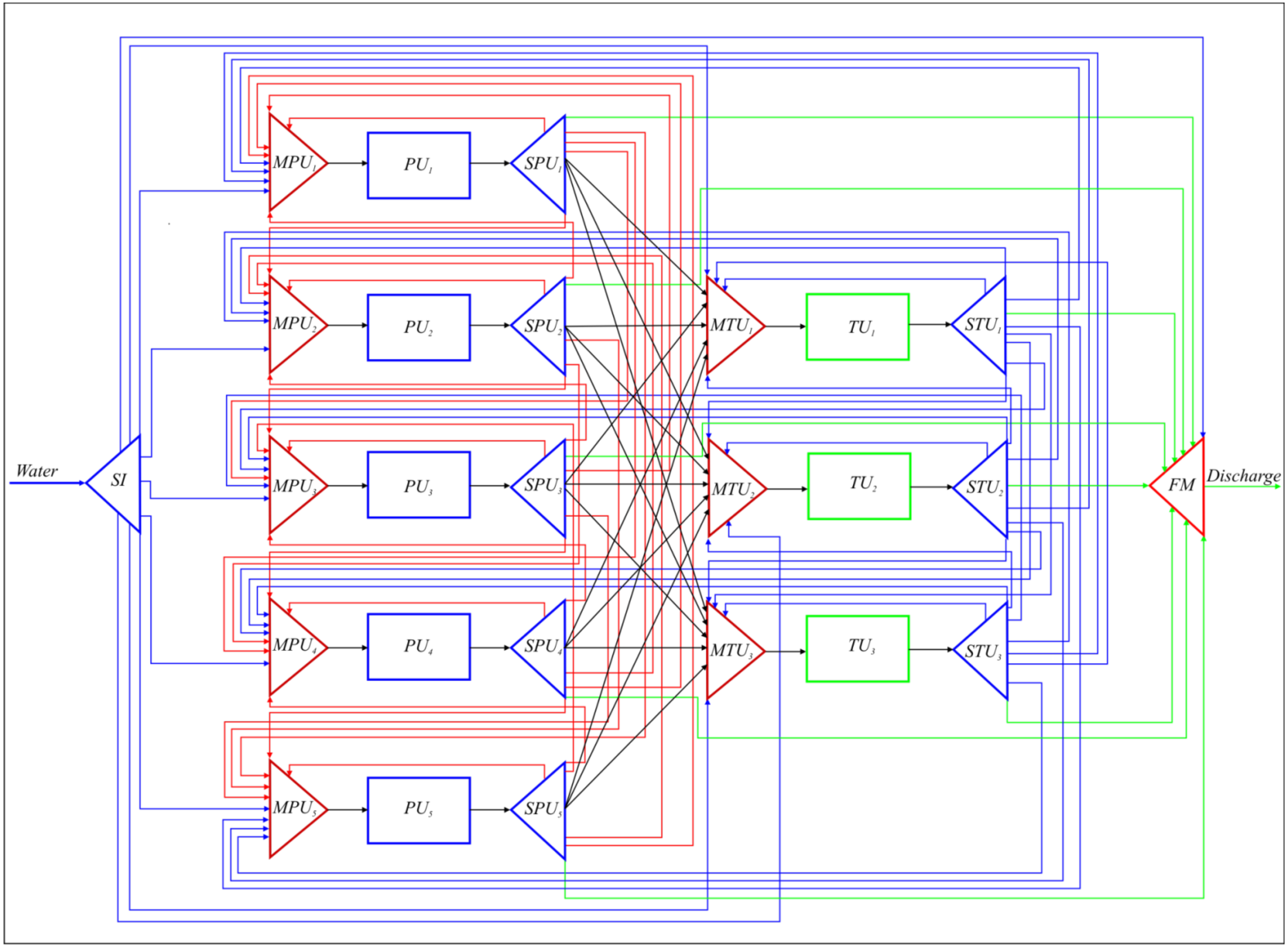
Splitter mass balances
Mixer mass balances (bilinear)
Process units mass balances
Treatment units mass balances
Design constraints

0-1 variables for piping sections

Model can be solved to global optimality

Superstructure of the integrated water network

1 feed, 5 process units, 3 treatment units, 3 contaminants



MINLP: 72 0-1 vars, 233 cont var, 251 constr
BARON optcr=0.01 197.5 CPUsec

Optimal design of the simplified water network with 13 removable connections

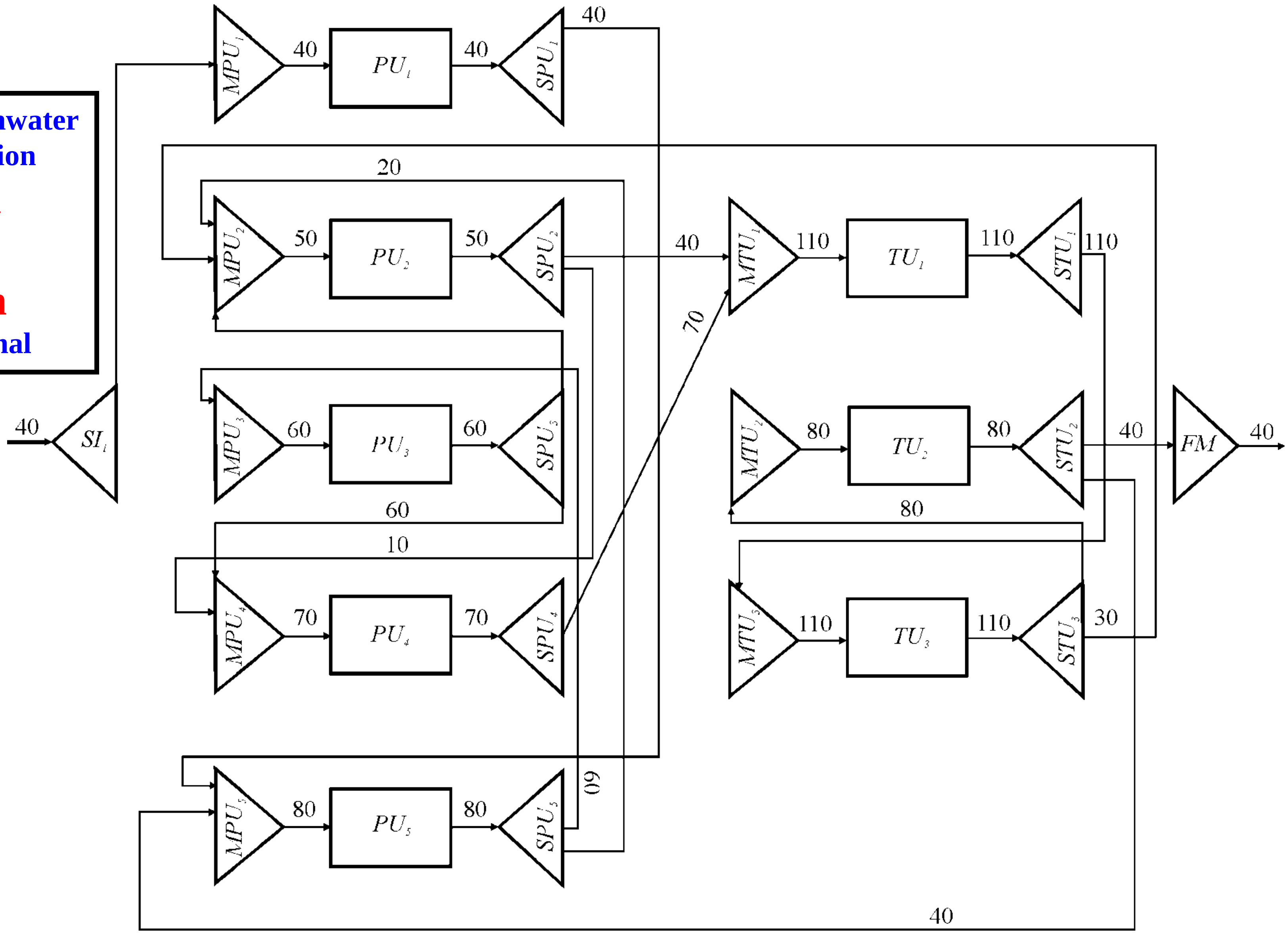
Optimal Freshwater Consumption

40 t/h

vs

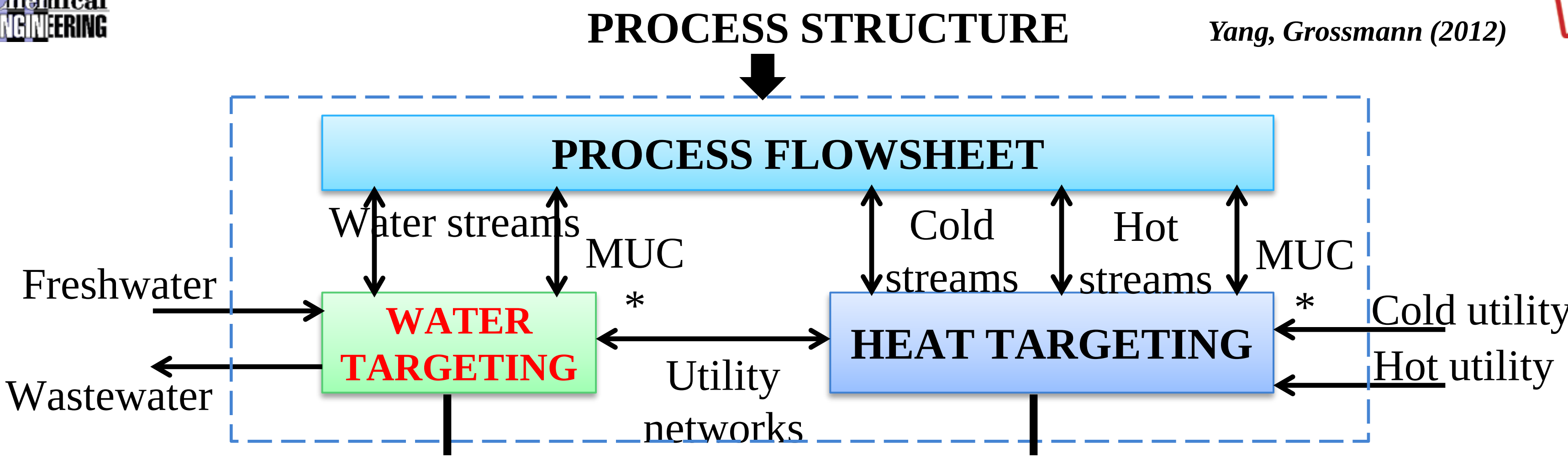
300 t/h

conventional



Simultaneous optimization heat and water integration

Yang, Grossmann (2012)



$$\min.\ \phi = F(x,u,v) + \sum_{i \in HU} c_H^i Q_H^i + \sum_{j \in CU} c_C^j Q_C^j + c_{fw} F_{fw}$$

$$\text{s.t. } h(x,u,v) = 0$$

$$g^P(x,u,v) \le 0$$

$$g^{HEN}(u, Q_H, Q_C) \le 0$$

Heat targeting: Duran & Grossmann (1986)

$$g^{WN}(v, F_{fw}) \le 0$$

Need Water Targeting Model

$$x \in X, \quad u \in U, \quad v \in V$$

Novel freshwater LP targeting formulation

Goal: determine minimum freshwater consumption

$$\min \quad Z = F_{fw}$$

$$\text{s.t.} \quad F^k = \sum_{i \in m_{in}} F^i \qquad \forall m \in MU, k \in m_{out}$$

$$F^k C_j^{k,\max} \geq \sum_{i \in m_{in}} F^i C_j^{i,\max} \qquad \forall j, \quad \forall m \in MU, k \in m_{out}$$

Mixer mass balances

$$F^k = \sum_{i \in s_{out}} F^i \qquad \forall s \in SU, k \in s_{in}$$

$$C_j^k = C_j^i \qquad \forall j, \quad \forall s \in SU, \qquad \forall i \in s_{out}, k \in s_{in}$$

Splitters mass balances

$$P_{in}^p C_j^k + L_j^p = P_{out}^p C_j^i \qquad \forall j, \forall p \in PU, i \in p_{out}, k \in p_{in}$$

Process unit mass balances

$$C_j^{k,\min} \leq C_j^k \leq C_j^{k,\max} \qquad \forall j, k$$

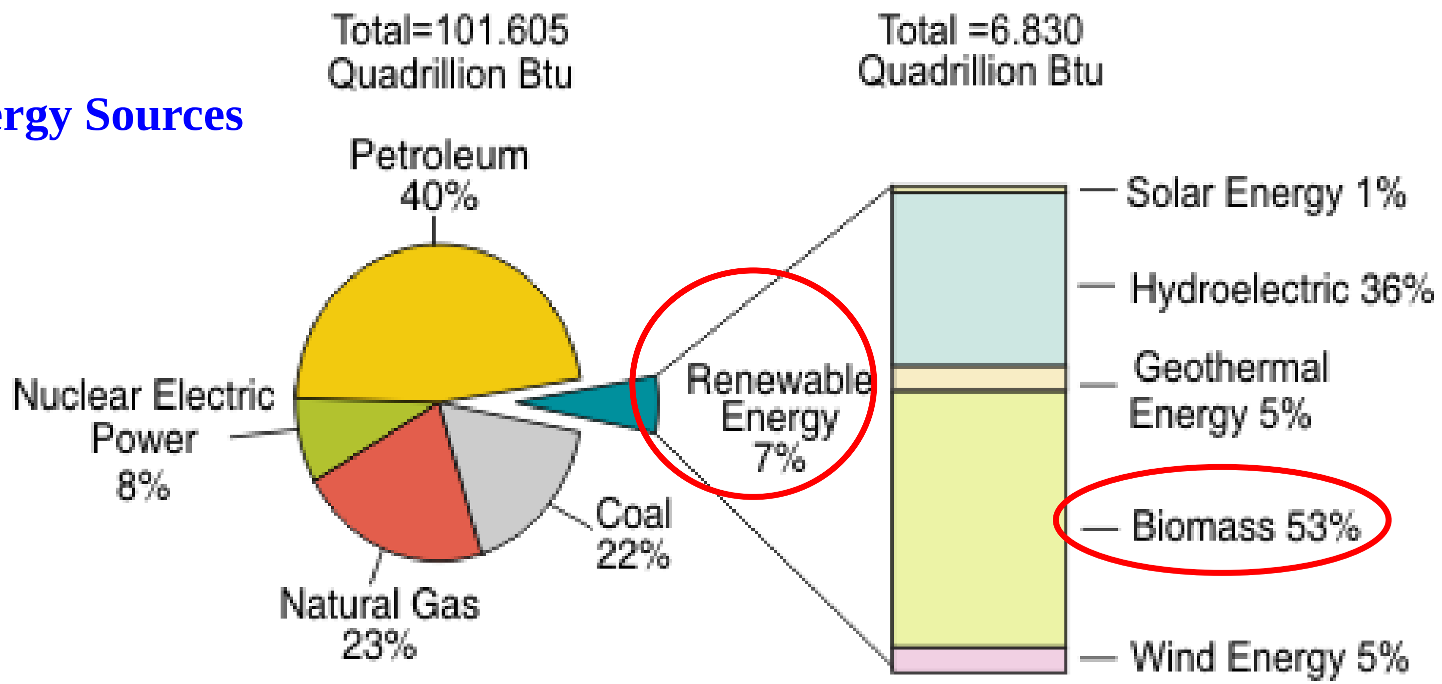
$$F^{k,\min} \leq F^k \leq F^{k,\max} \qquad \forall k$$

Proposition: *The* ***minimum freshwater consumption predicted by the LP model is the same as the global minimum predicted by the NLP*** *model under the condition that at least one contaminant reaches its concentration upper bounds as well as at all other process units from which reuse streams have non-zero flowrate.*

LP targeting formulation provides either exact target or tight upper bound

Biomass an important renewable

US Energy Sources



Note: Sum of components may not equal 100 percent due to independent rounding.
Source: EIA, *Renewable Energy Consumption and Electricity Preliminary 2007 Statistics*, Table 1: U.S. Energy Consumption by Energy Source, 2003-2007 (May 2008).

Scope of Advanced Process Systems Engineering Tools

Energy consumption corn-based process

Author (year)	Energy consumption (Btu/gal)
Pimentel (2001)	75,118
Keeney and DeLuca (1992)	48,470
Wang et al. (1999)	40,850
Shapouri et al. (2002)	51,779
Wang et al (2007)	38,323

From Karrupiah et al (2007)
24,918 Btu/gal vs 38,323 Btu/gal
Why? ***Multieffect distillation and heat integration***

Water consumption corn-based process

Author (year)	Water consumption (gal/gal ethanol)
Gallager (2005) First plants	11
Philips (1998)	5.8
MATP (2008) Old plants in 2006	4.6
MATP (2008) New plants	3.4

From Martin and Grossmann (2010)
1.5 gal water/gal ethanol vs 3.4
Why? ***Integrated process network with reuse and recycle***

Proposed Design Strategy for Energy and Water Optimization

Energy optimization

Issue: fermentation reactions at modest temperatures

=> No source of heat at high temperature as in petrochemicals

Multieffect distillation followed by heat integration process streams

Water optimization

Issue: cost contribution is currently still very small (freshwater contribution < 0. 1%)

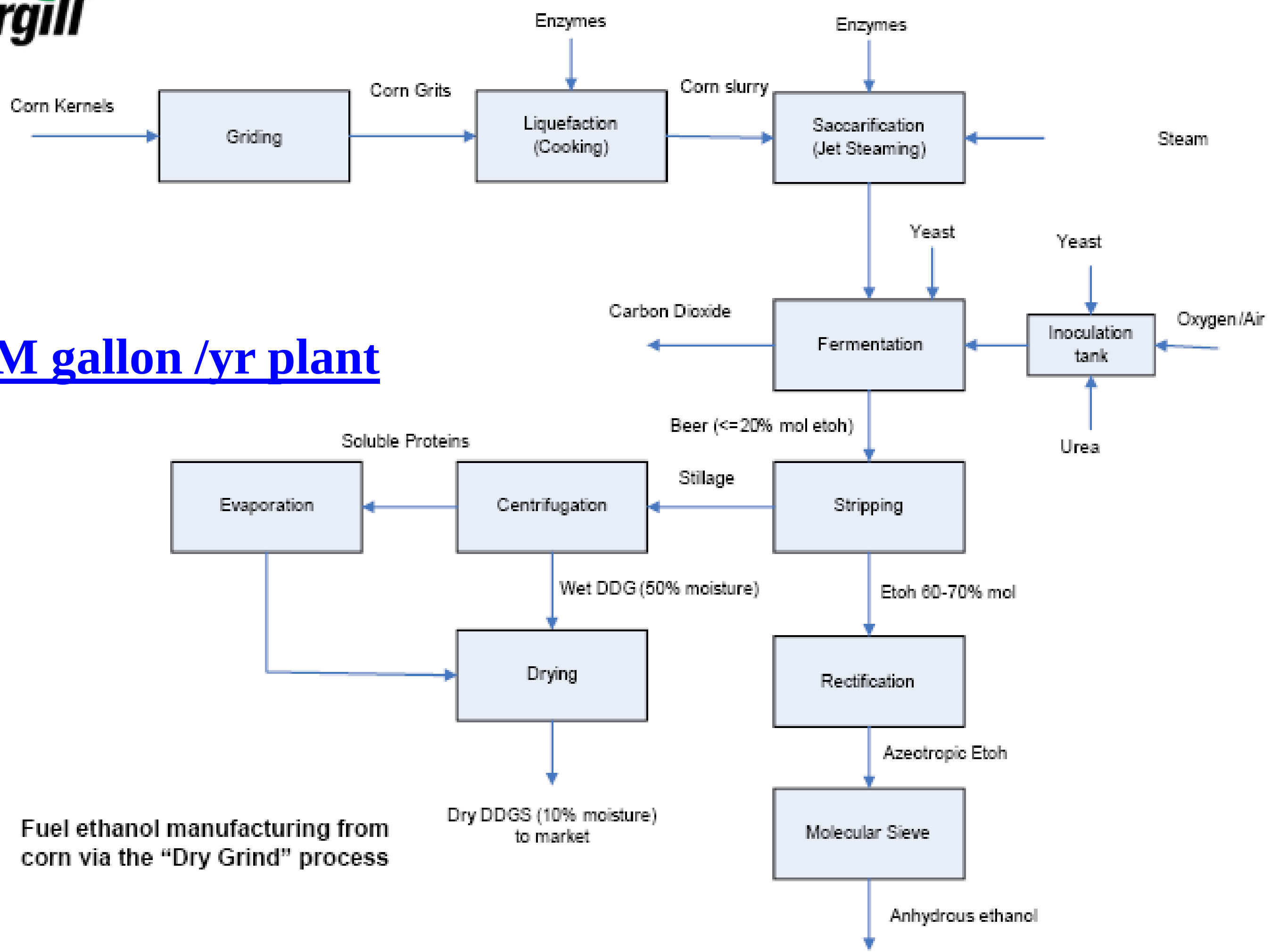
=> Total cost optimization is unlikely to promote water conservation

Optimal process water networks for minimum energy consumption

Energy Optimization of Corn-based Bioethanol

Peschel, Martin, Karuppiah, Grossmann, Zullo, Martinson (2007)

Cargill



60 M gallon /yr plant

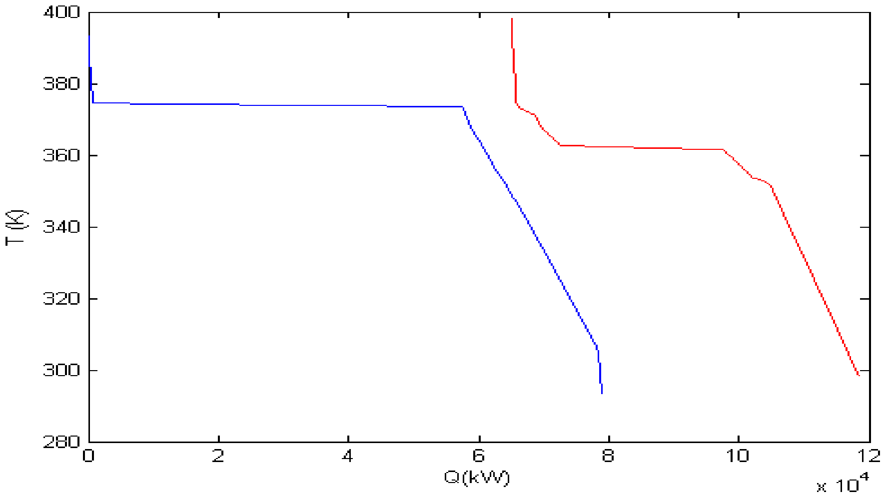
Fuel ethanol manufacturing from corn via the "Dry Grind" process

Equipment cost = M$ 18.4   **Steam cost = M$ 21/yr**

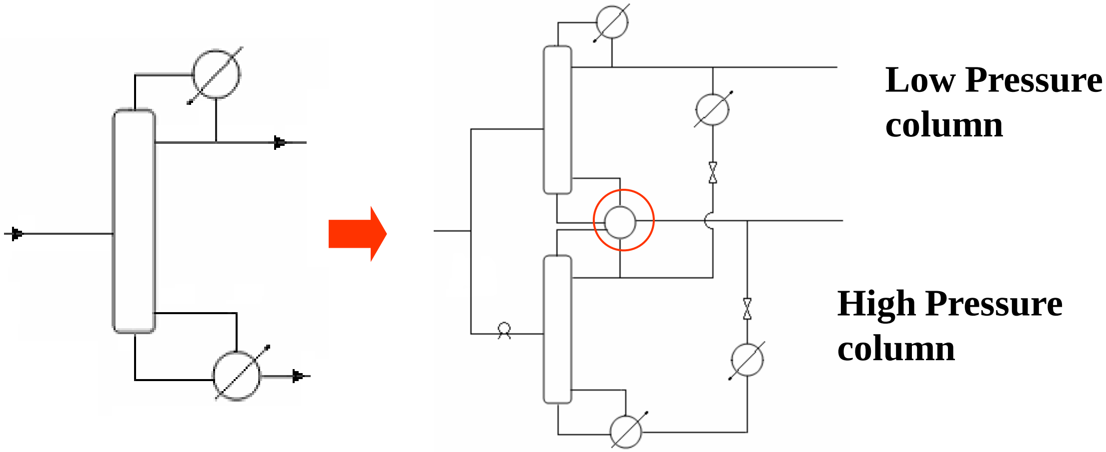
Prod. cost = 1.50 $/gal

Alternatives for Energy Reduction

Heat Integration process streams:



Multieffect columns:

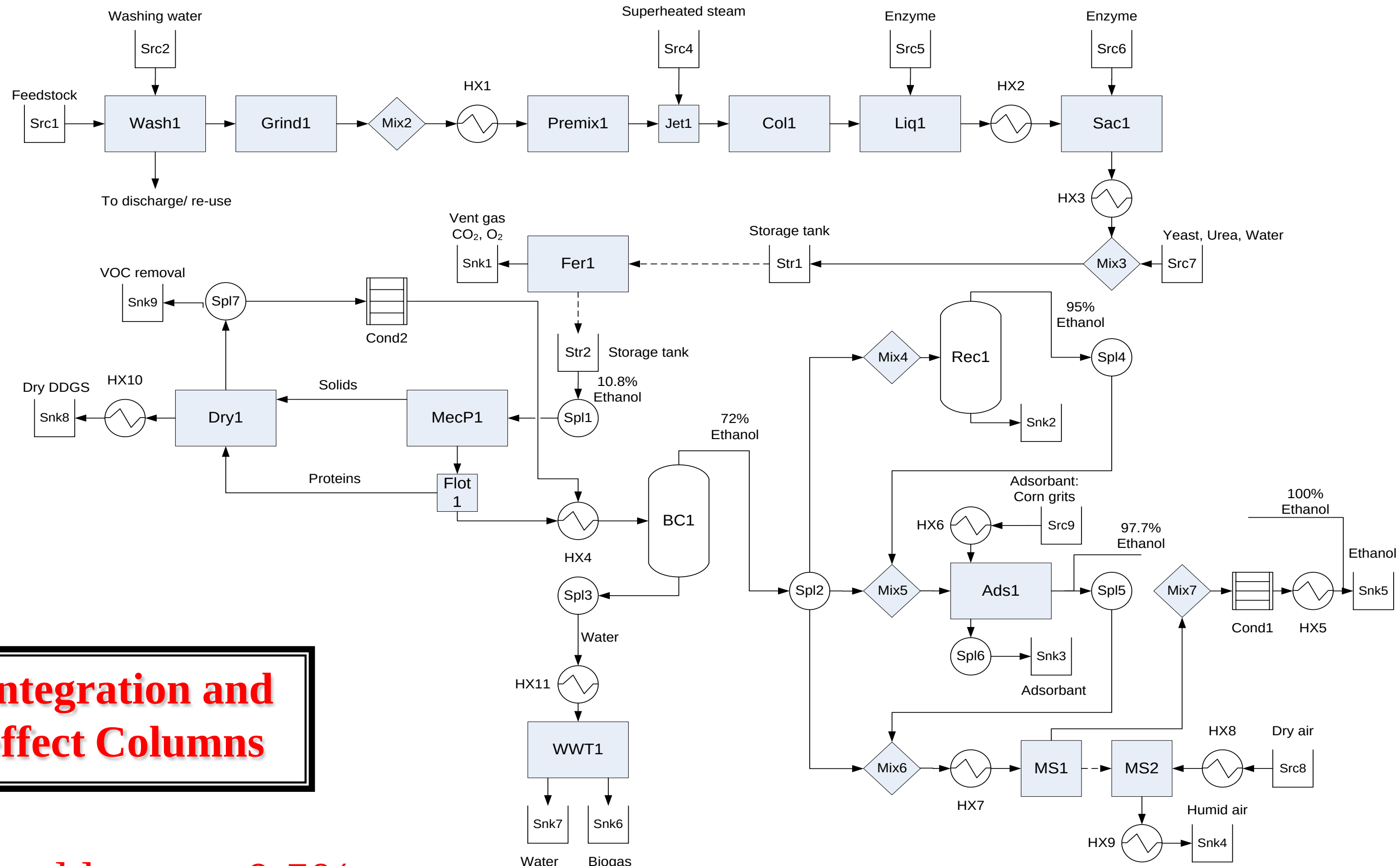


GDP model comprises mass, energy balances, design equations *(short cut)*

2,922 variables (2 Boolean) 2,231 constraints

Energy Optimal Design

60 M gallon /yr plant



Heat Integration and Multieffect Columns

Ethanol losses : 0.5%

Equipment cost = **M$ 20.7**

Steam cost = **M$ 7.1/yr (-66%)**

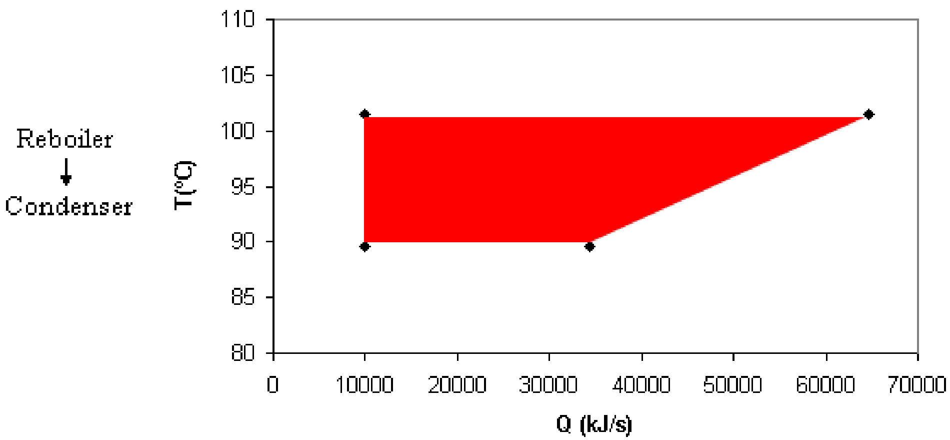
Prod. cost = 1.28 **$/gal**

Reduction from $1.50/gal (base case) to $1.28/gal !

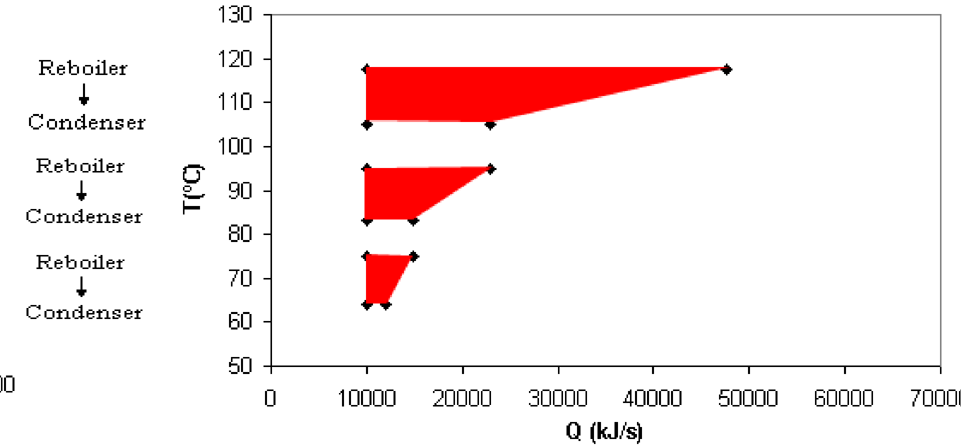
Energy Profiles in Multieffect Columns

Beer Column

Single column

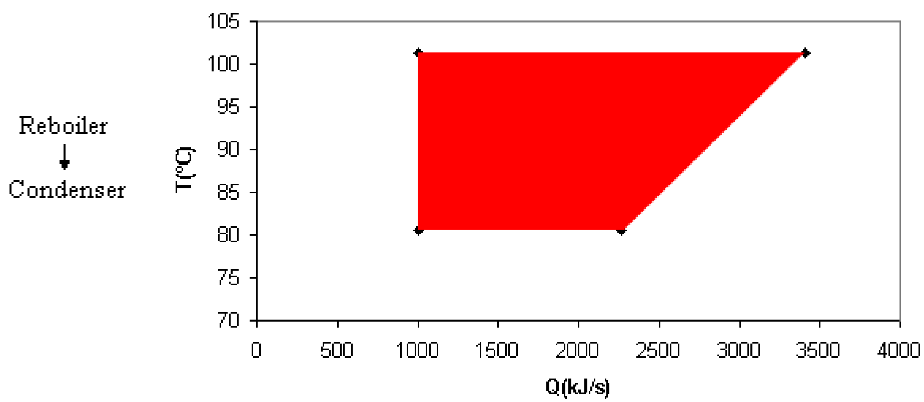


Triple effect column

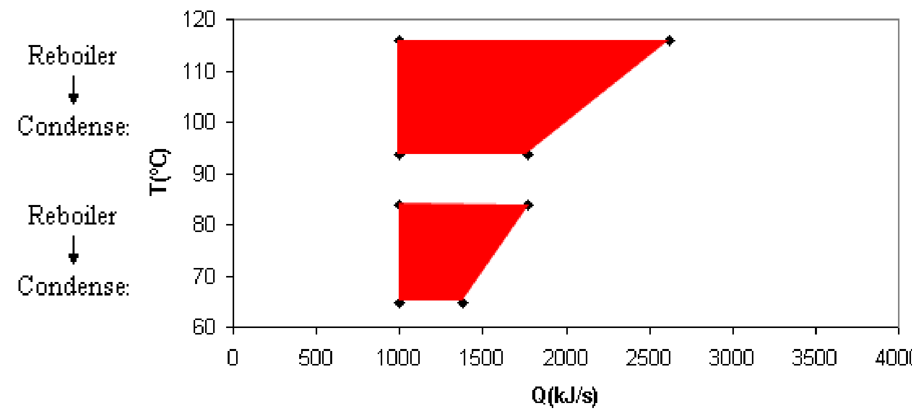


Rectification Column

Single column



Double effect column

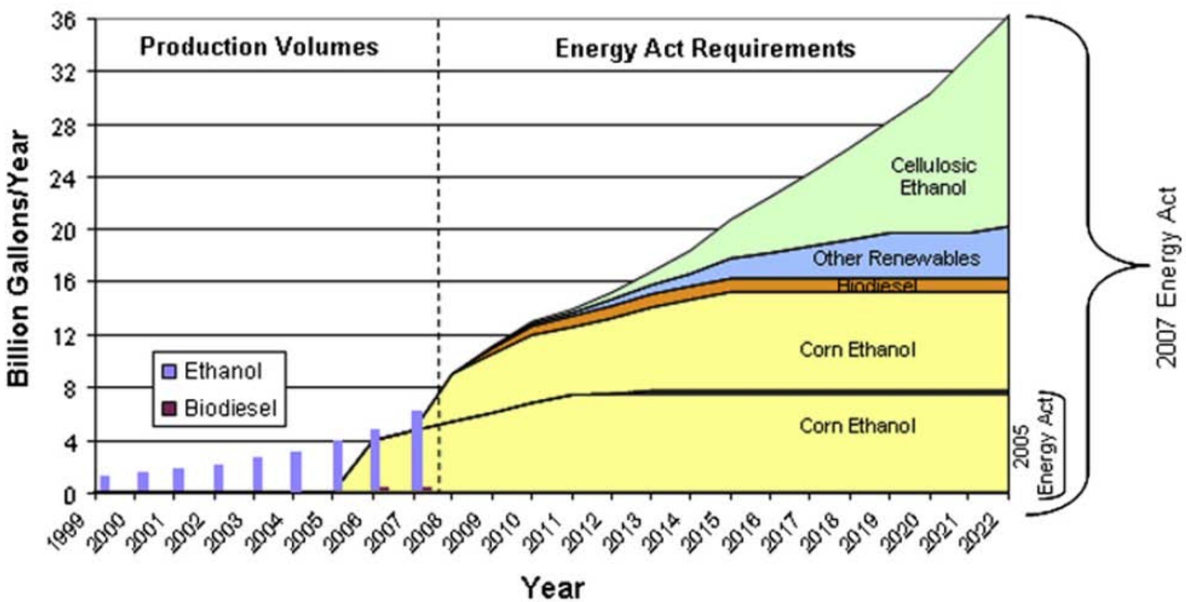


24,918 Btu/gal vs 38,323 Btu/gal

Remarks

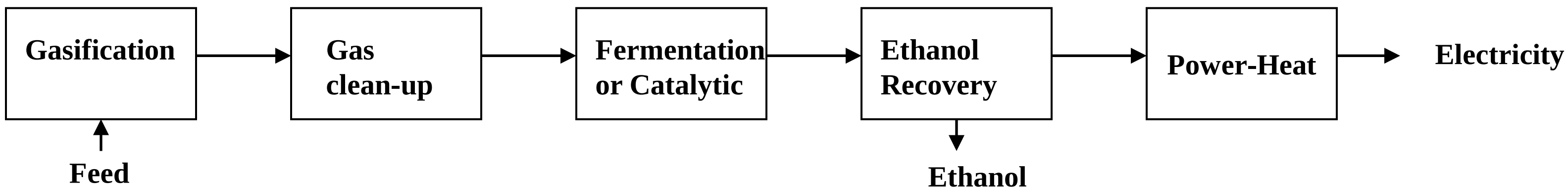
Current ethanol from corn and sugar cane and biodiesel from vegetable oils compete with the food chain.

U.S. Government policies support the production of lignocellulosic based biofuels and the reuse of wastes and new sources (algae)

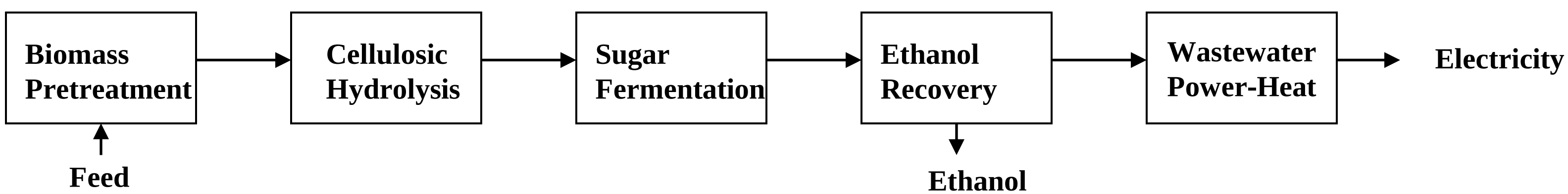


Lignocellulosic Bioethanol

a) Thermochemical Process *(gasification)*



b) Hydrolysis Process *(fermentation)*



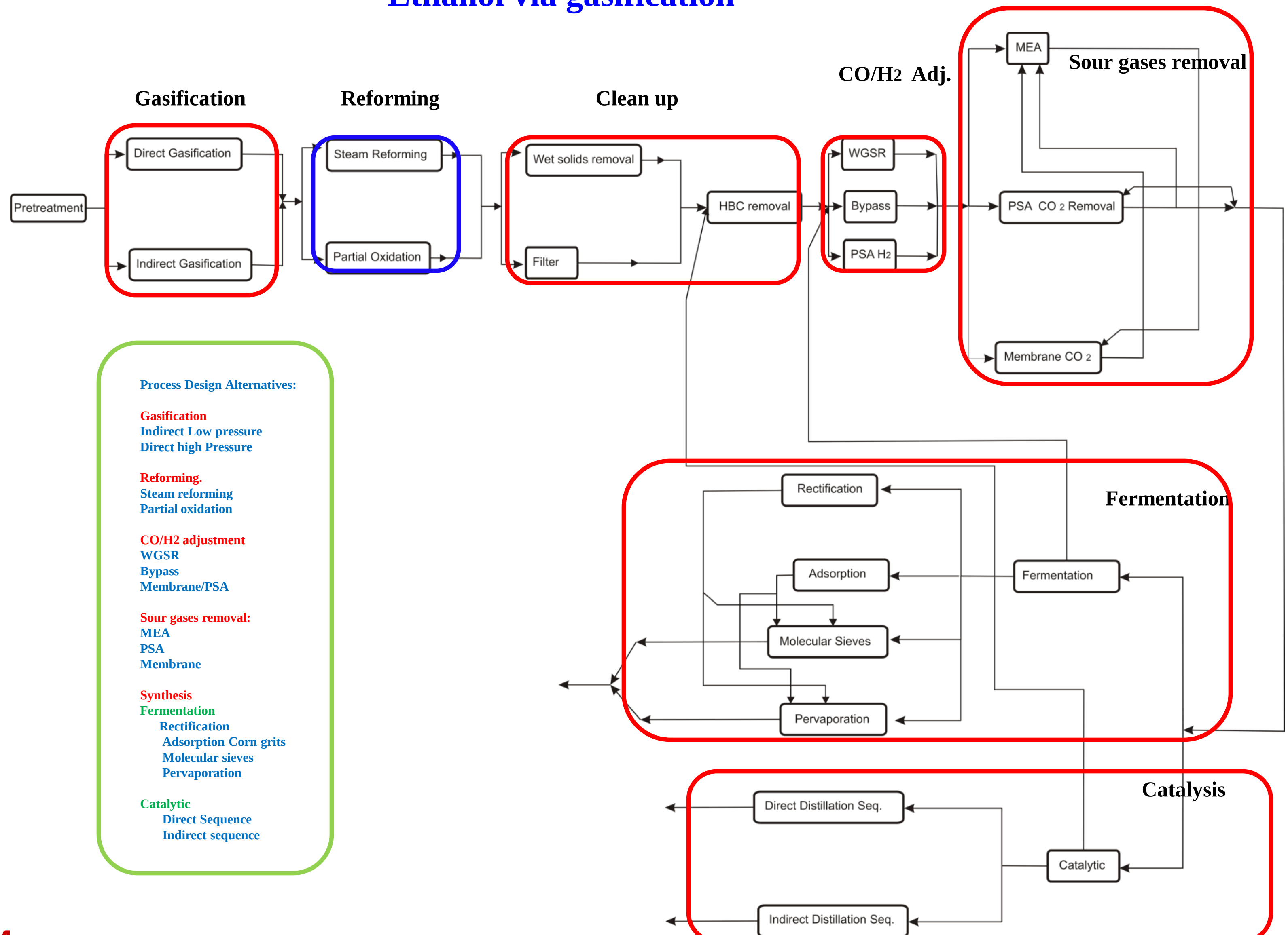
Challenge:

<u>Many alternative flowsheets</u>

Superstructure Thermochemical Bioethanol

Martin, Grossmann (2010)

Ethanol via gasification



Process Design Alternatives:

Gasification
Indirect Low pressure
Direct high Pressure

Reforming.
Steam reforming
Partial oxidation

CO/H2 adjustment
WGSR
Bypass
Membrane/PSA

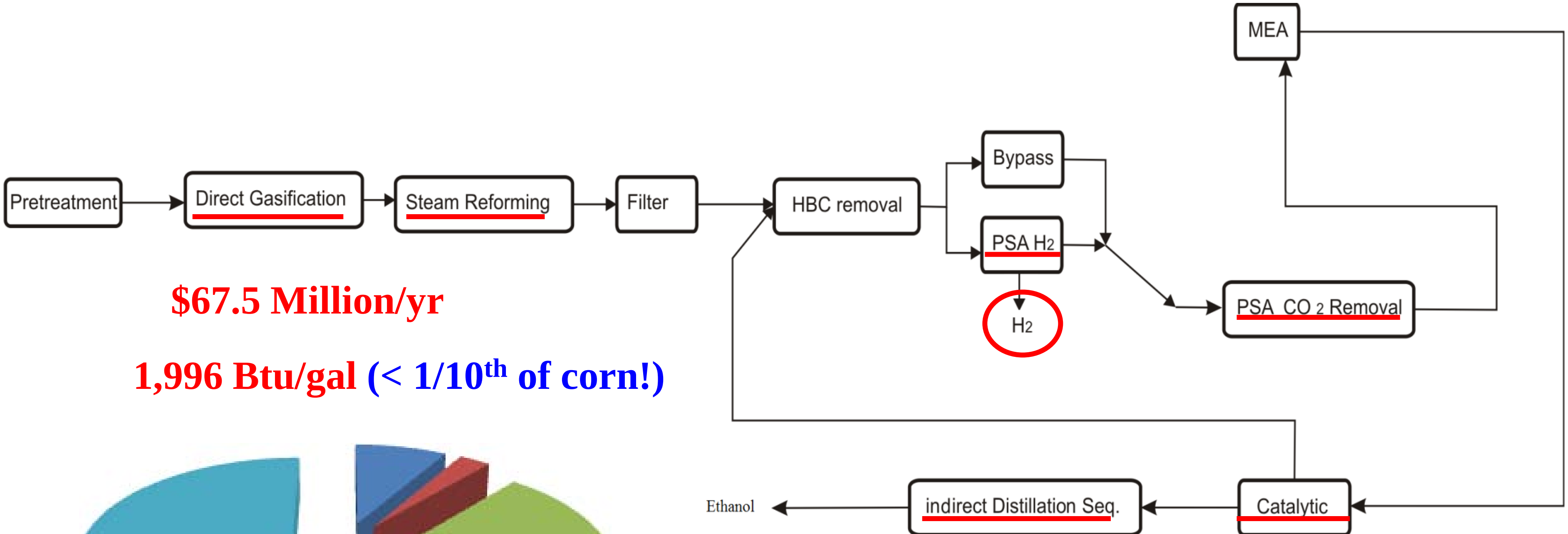
Sour gases removal:
MEA
PSA
Membrane

Synthesis
Fermentation
- **Rectification**
  - **Adsorption Corn grits**
  - **Molecular sieves**
  - **Pervaporation**

Catalytic
- **Direct Sequence**
- **Indirect sequence**

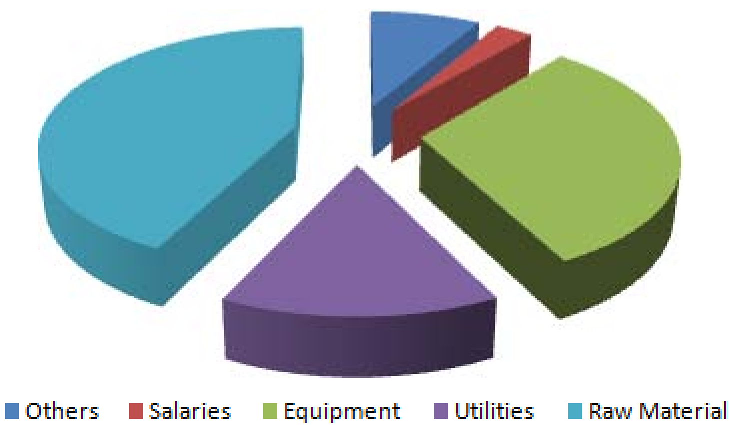
-Martin, M. Grossmann, I. E (2010) Aiche J. Submitted

Optimal Design of Lignocellulosic Ethanol Plant



$67.5 Million/yr

1,996 Btu/gal (< 1/10th of corn!)



Ethanol: $0.81 /gal *(no H_2 credits)*
$ 0.42/gal *(H_2 credits)*

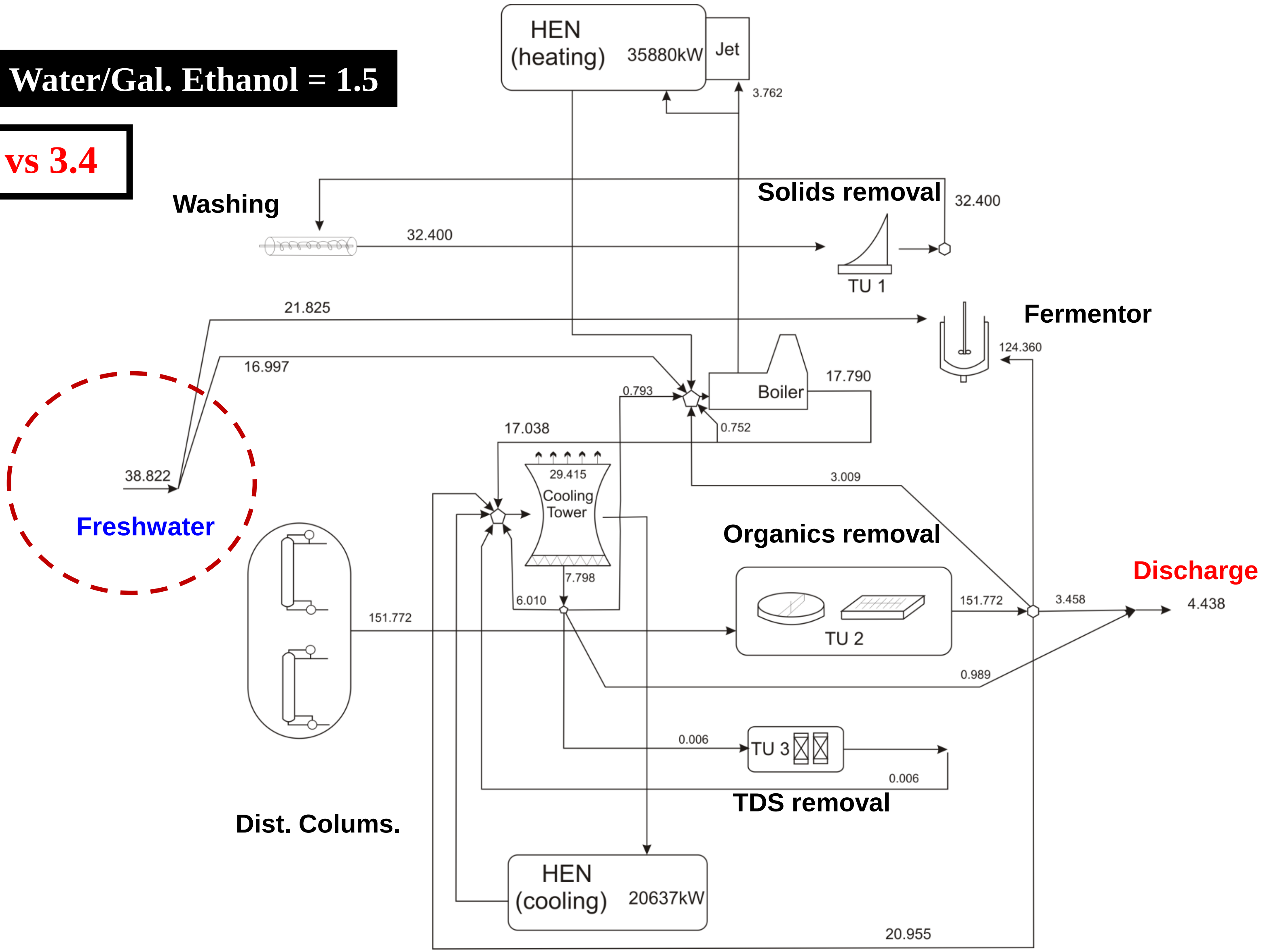
Low cost is due to H_2 production

Each NLP subproblem: 7000 eqs., 8000 var
~25 min to solve

Optimal Water Network: Corn Ethanol

Gal. Water/Gal. Ethanol = 1.5

1.5 vs 3.4

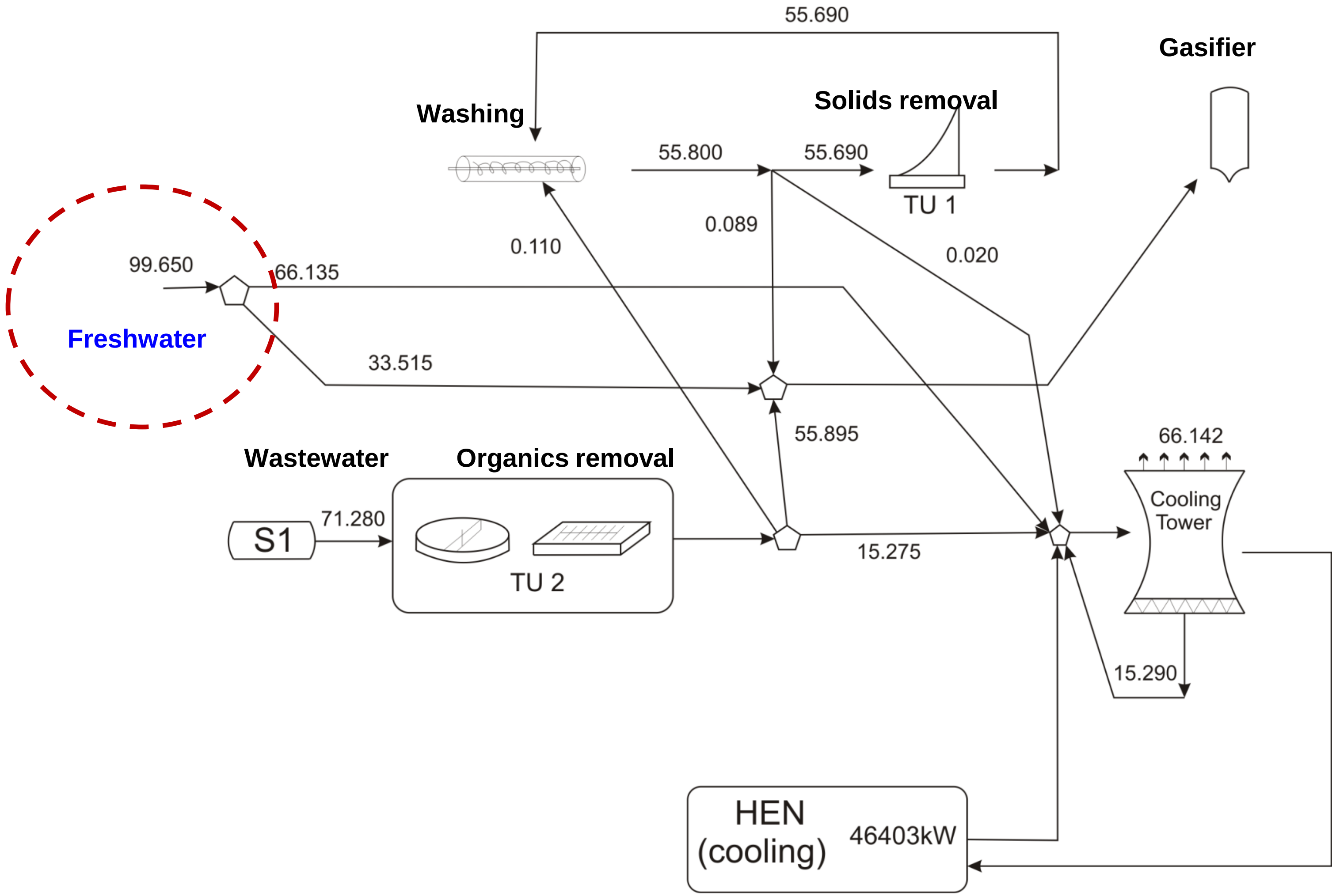


-Ahmetović , E., Martin, M. Grossmann, (2009) I&ECR. **2010, *49, 7972–7982***

Optimal Water Network: Lignocellulosic Ethanol

Gal. Water/Gal. Ethanol = 4.2

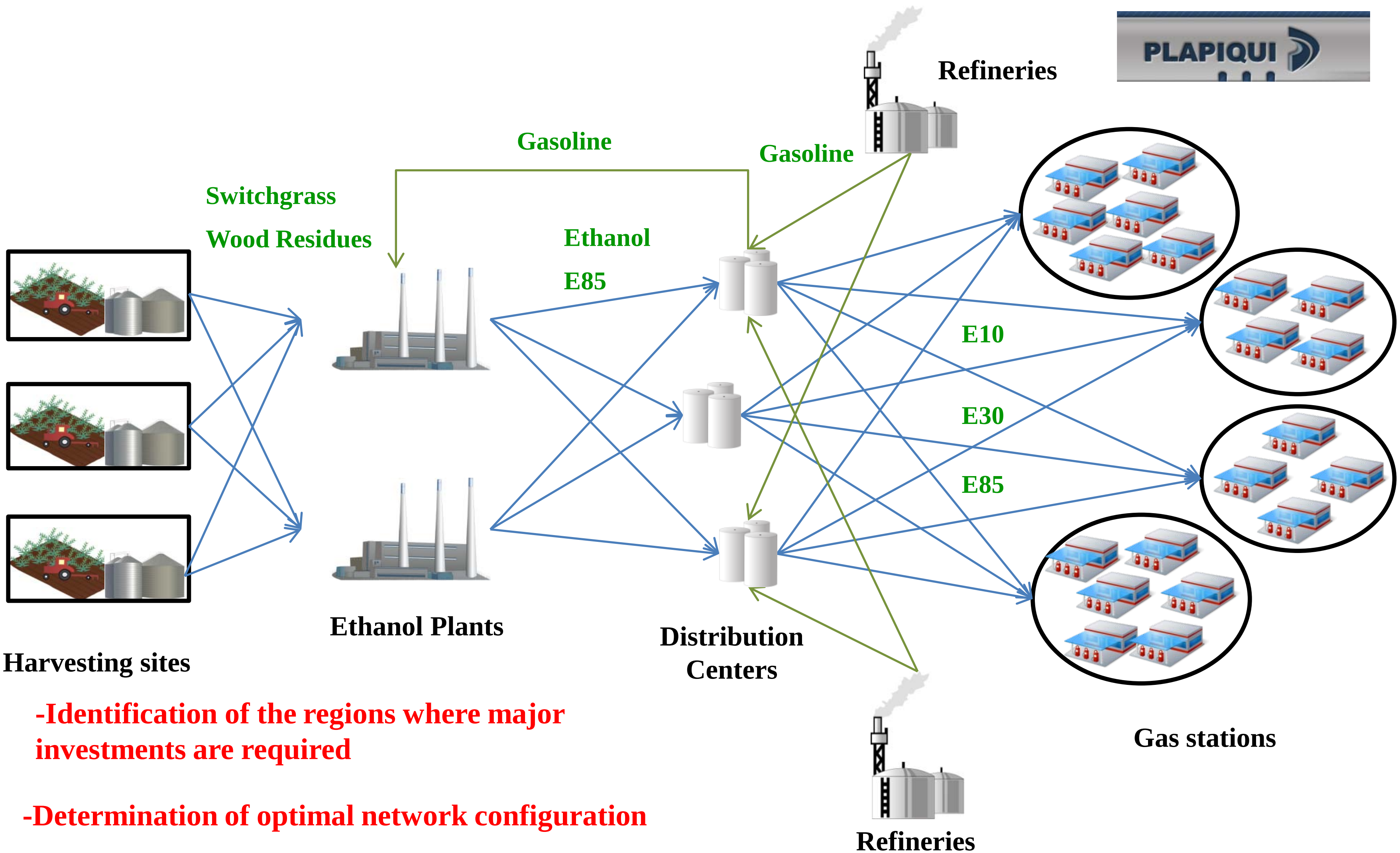
Cellulosic Bioethanol via Gasification



-Martin, M. , Ahmetović, E., Grossmann, I. E (2010) I&ECR ASAP

Strategic Planning for the Design of Integrated Ethanol and Gasoline Supply Chain

Andresen, Diaz, Grossmann (2012)



-Identification of the regions where major investments are required

-Determination of optimal network configuration

PROBLEM STATEMENT

✓ Simplified Strategic Planning model
Detailed Strategic Planning model

<u>Given</u>:

- ✓ ***Superstructure***
- ✓ ***Multiperiod model*** **with time horizon of 20 years.**
- ✓ **Means of transportation → truck, railway and pipeline (for gasoline)**
- ✓ ***Existing capacity*** **for ethanol plants (EP) and gasoline distribution center (GDC)**
- ✓ ***Potential capacity*** **for EP and GDC**
- ✓ **Fixed and variable *investment and operation costs***
- ✓ ***Number of Existing Gas Stations***
- ✓ ***Feasible Set of Retrofits***
- ✓ ***Forecast of demand*** **for different blends over entire time horizon according to each region population**
- ✓ ***Economy of Scale*** **for capital investment (small – medium – large sizes) – not in Gas Stations**

<u>Determine</u>:

- ✓ **Whether to *install, expand or not* EP and GDC**
- ✓ **Timing profile of different types of Gas Stations in each Region**
- ✓ **New Gas Stations and Retrofits over them to comply with blends demand**
- ✓ ***Flows in network*** **for each time period**

PROBLEM FORMULATION

Multiperiod MILP Model

Objective function: *min COST*

Subject to:
Mass Balances
Capacity constraints
Transportation constraints
Inventory level constraints
Gas Stations Model
Capital investment
Fixed and variable operation cost
Demand at Retail Center

0-1 variables for investments on harvesting sites / ethanol plants / distribution centers

Integer variables for number of Gas Stations

Example: Supply Blends in Alabama

MILP: 1400 0-1, 136,000 cont. var.
109,000 constraints

Data

Raw Materials

Wood Residues – Switchgrass

Products

E10 – E30 – E85

Transportation Modes

Truck – Railway – Pipeline (only for gasoline)

Ethanol Technologies

Biochem – Thermochem – Hybrid (gasif+ferment)

Ethanol Plants & DC's Capacity

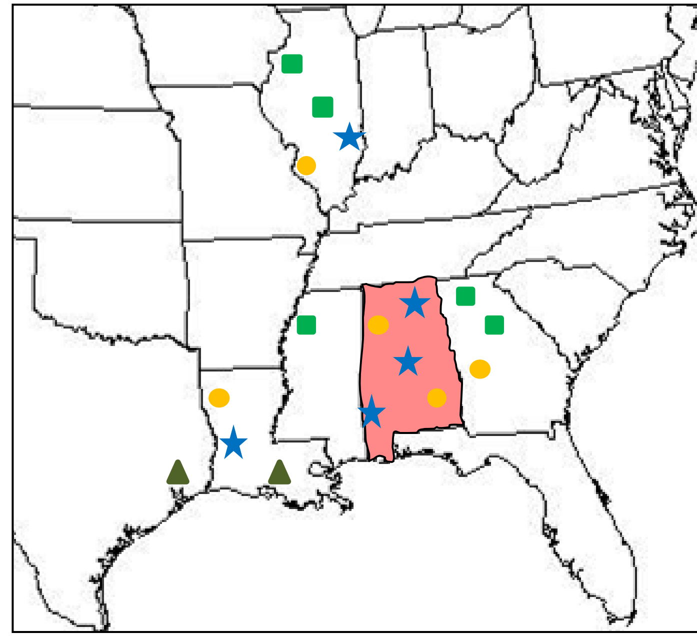
Low – Medium - Large

Existing number of GS in all Alabama state

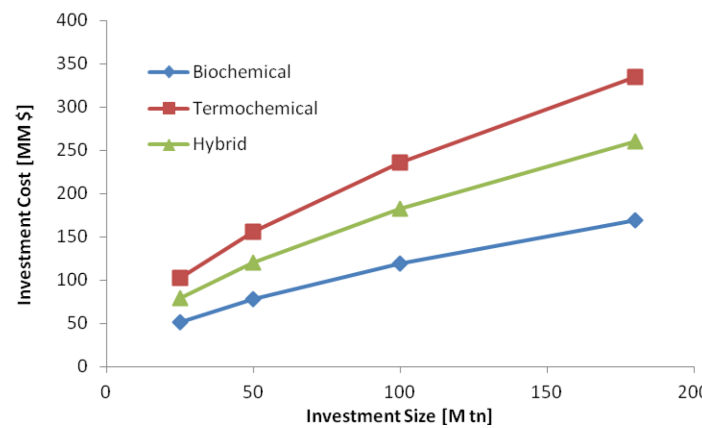
2,219 (G1) – 315 (G2) – 134 (G3)

Total SC Cost

Capital cost – Purchase cost (gasoline) – Distribution cost
Production cost – Transportation cost – Inventory cost

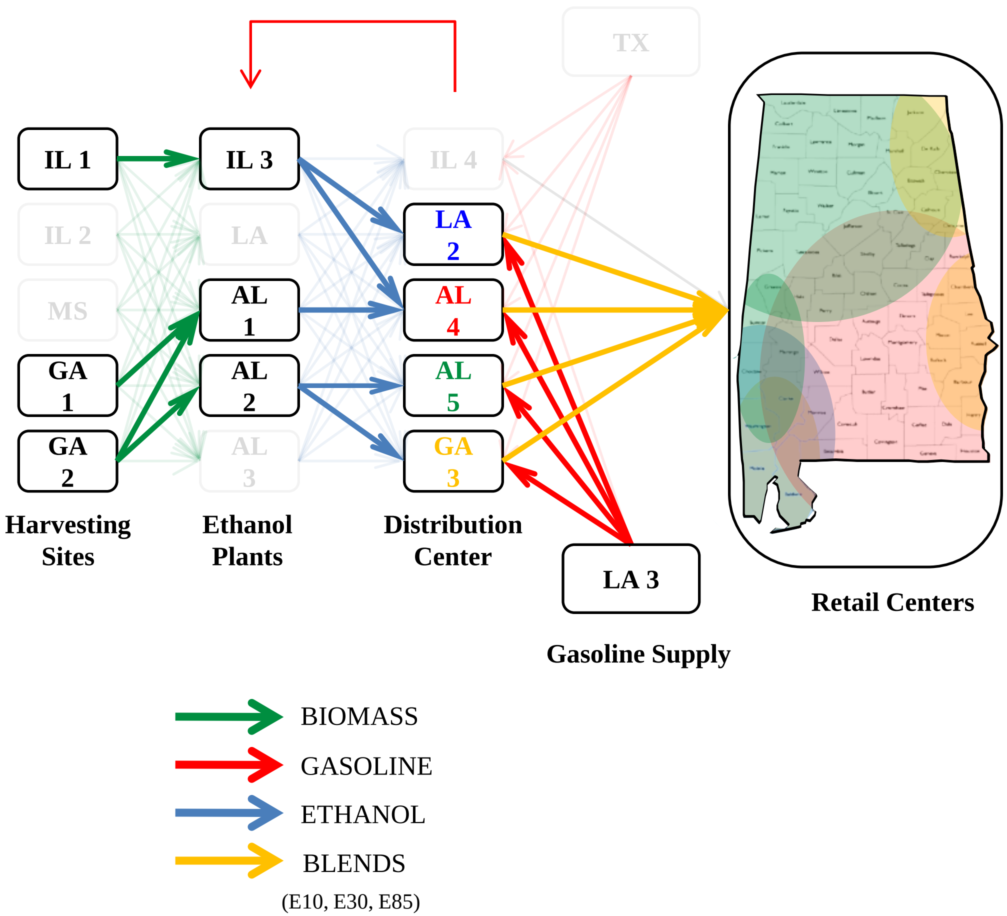


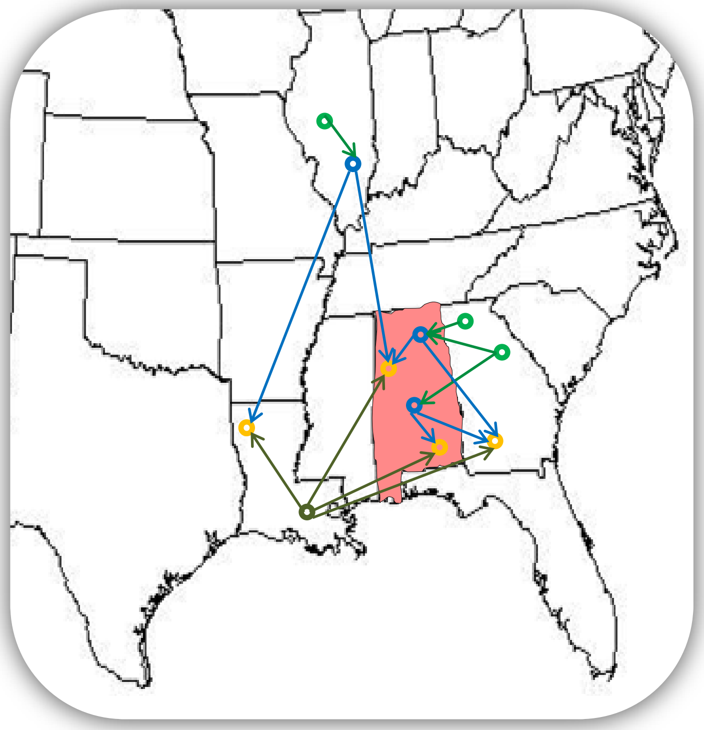
- Harvesting Sites
- Ethanol Plants
- Distribution Centers
- Retail Centers
  AL counties (76)
- Refineries



Results

Geographical information





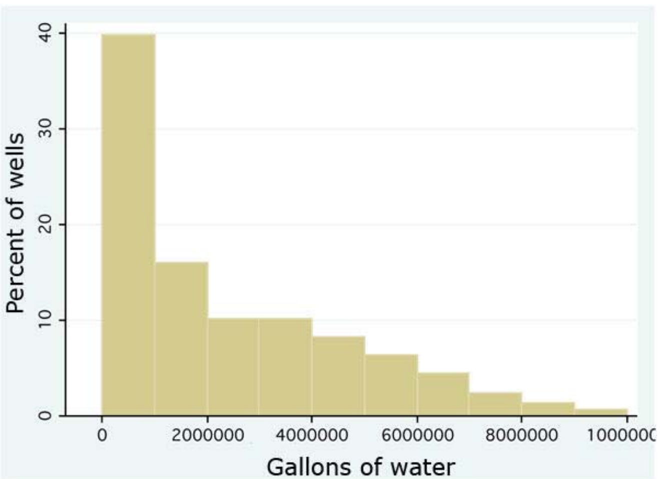
- 3 Harvesting Sites
- 3 Ethanol Plants
- 4 Distribution Centers
- 1 Gasoline Supply
- 67 Retail Centers

Water management in shale gas production

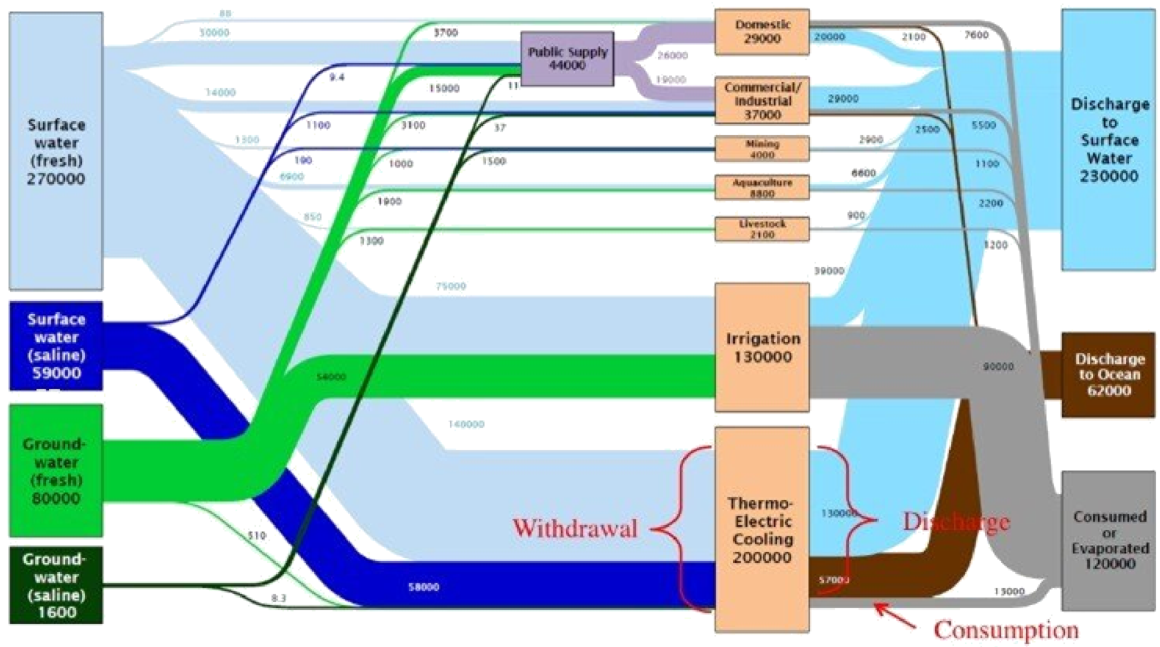
Yang, Grossmann (2014)

- » Concern 1: Large volume of water (3-5 MM gallons) to complete a well
  - Accounts for 0.1% of all freshwater ***withdrawal*** in the US[1]
- » Concern 2: Most water used (65-80%) in fracking for shale is consumed
  - Accounts for 0.3% of all water ***consumption*** in the US[1]

Distribution of water consumption per frack job[2]

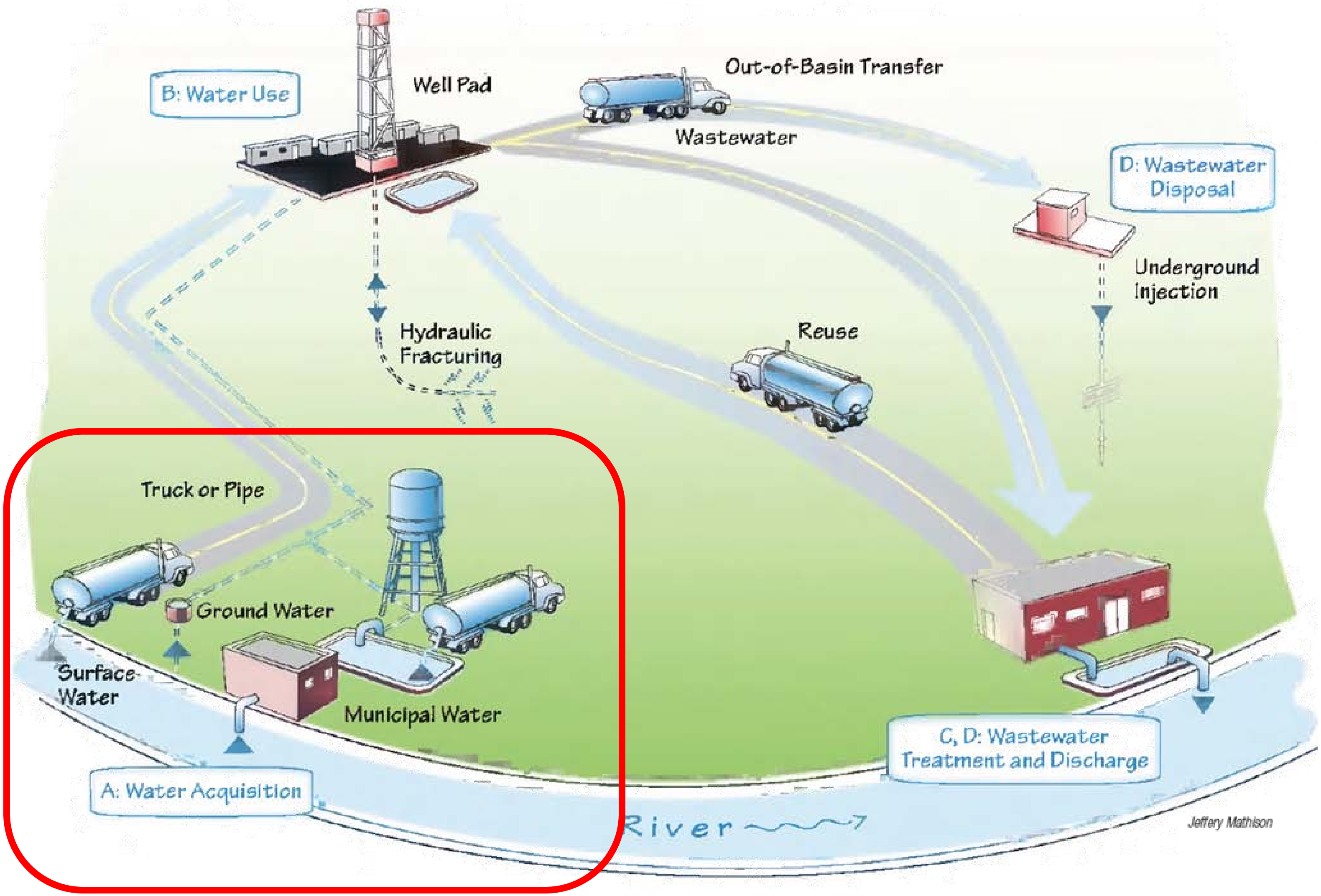


Freshwater water withdrawals in 2005



Units: MGal/Day

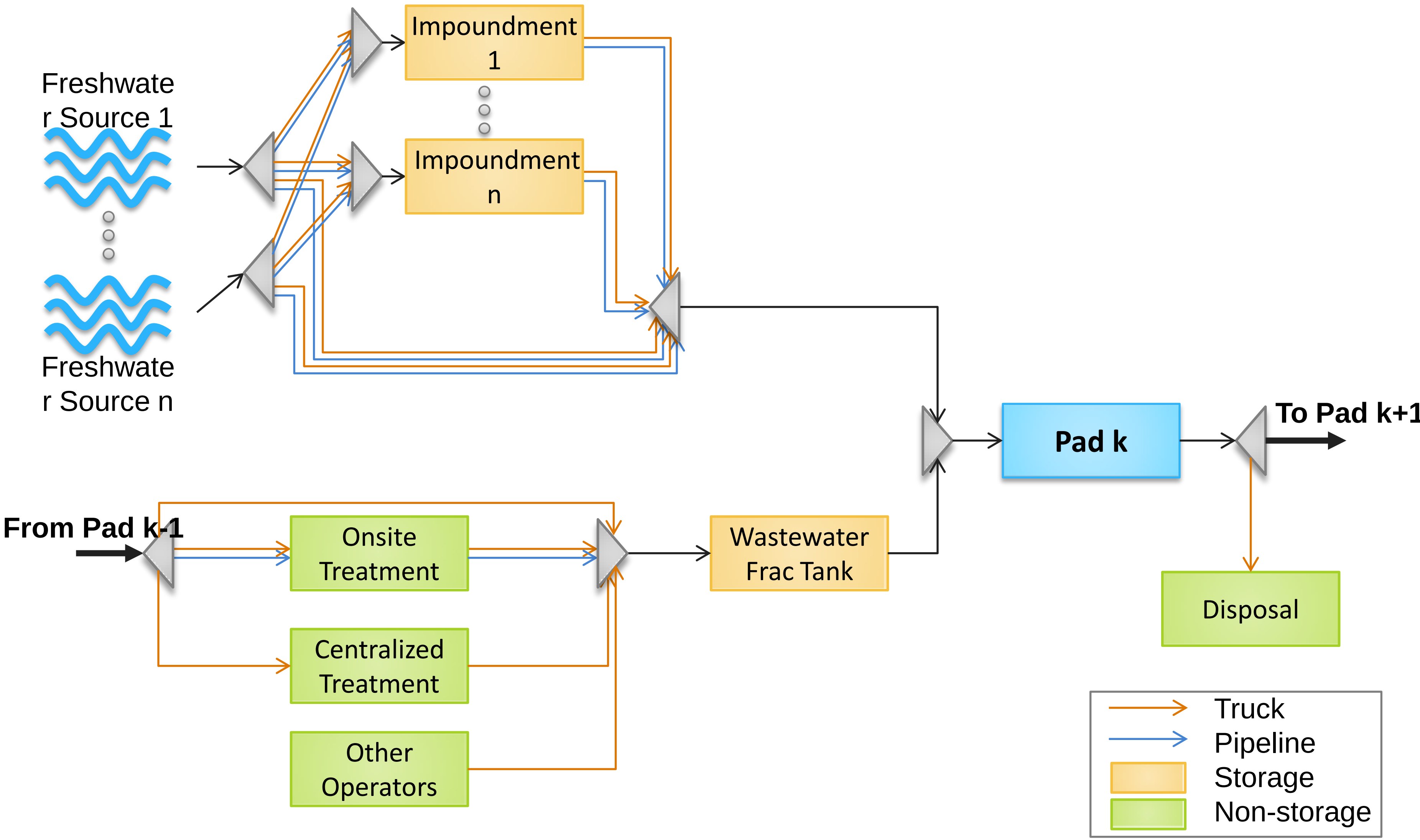
Water use logistics



Problem statement

- **Objective**
  - Minimize transportation cost, treatment cost, freshwater cost, and additional infrastructure cost
  - Maximize number of stages to be completed
- **Given**
  - Freshwater sources
  - Freshwater withdrawal data
  - Location of well pads
  - Location of treatment facilities
- **Determine**
  - Fracturing schedule & sequence
  - Additional impoundment
  - Additional treatment unit
  - Recycle ratio

Superstructure



Flowback flowrate and concentration

» Flowback volume is 15% of injected volume

» No bilinear terms (flow times concentration)

» Flowback rate and concentration profile are given

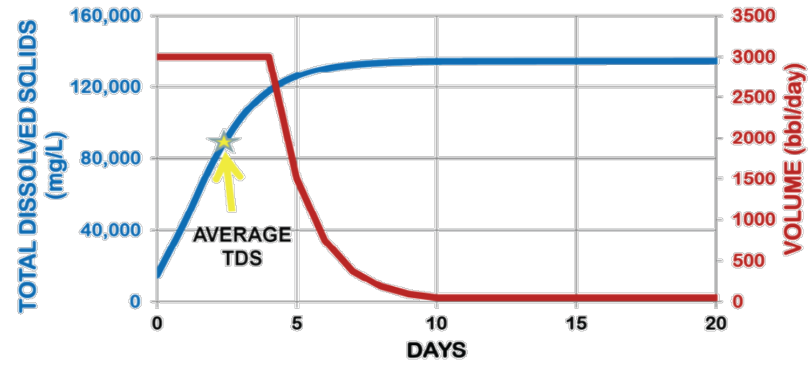
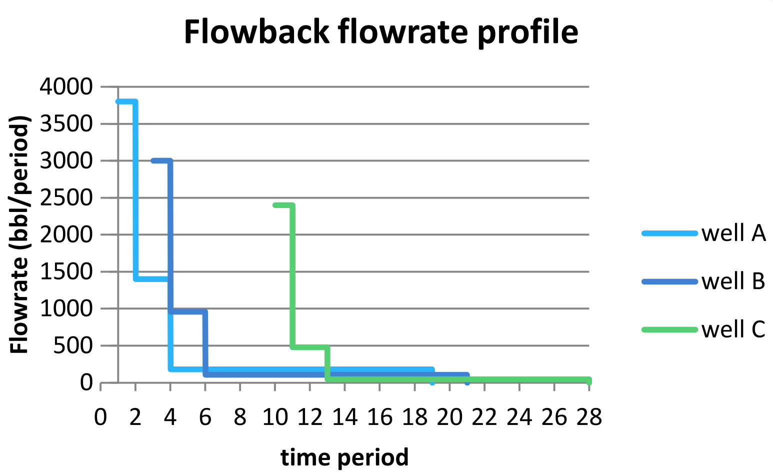
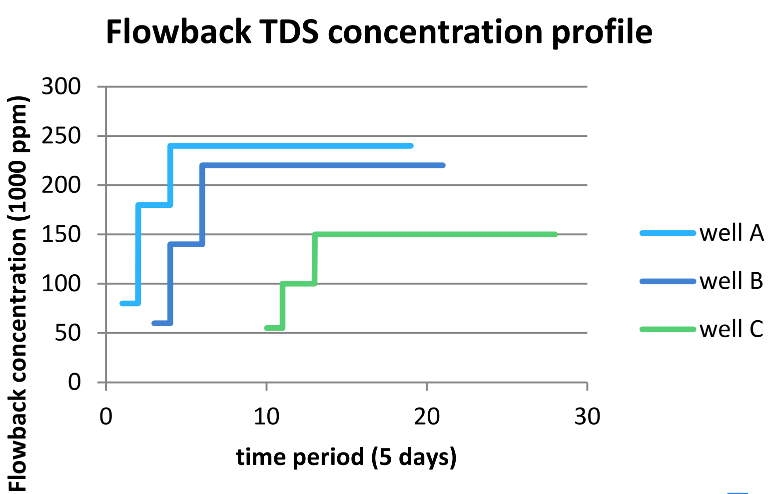
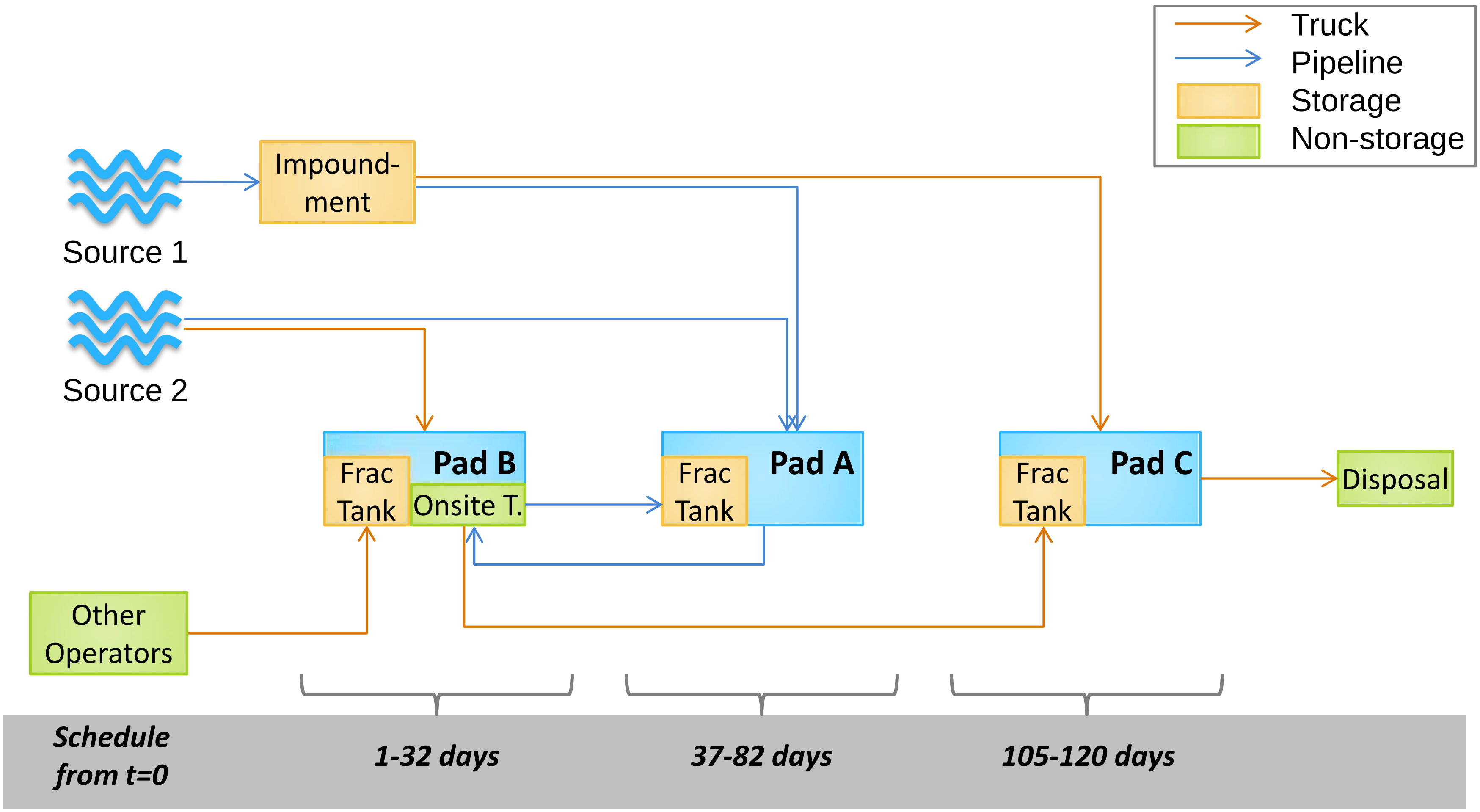


FIGURE 3.0: Example Flowback Volume vs. TDS Profile





Optimal Schedule



Sustainable Design and Planning of Hydrogen Supply Chains for Vehicle Use

Guillén-Gosálbez, Mele and Grossmann (2010)

Motivation

- **Motivation for the adoption of hydrogen:**

  Reduces well-to-wheel GHG gases emissions ***(Hugo et al., 2006)***

- **Major obstacle to achieve the hydrogen transition** ***(Jensen and Ross, 2000)***

  Developing an efficient infrastructure for producing and delivering hydrogen

Objective:

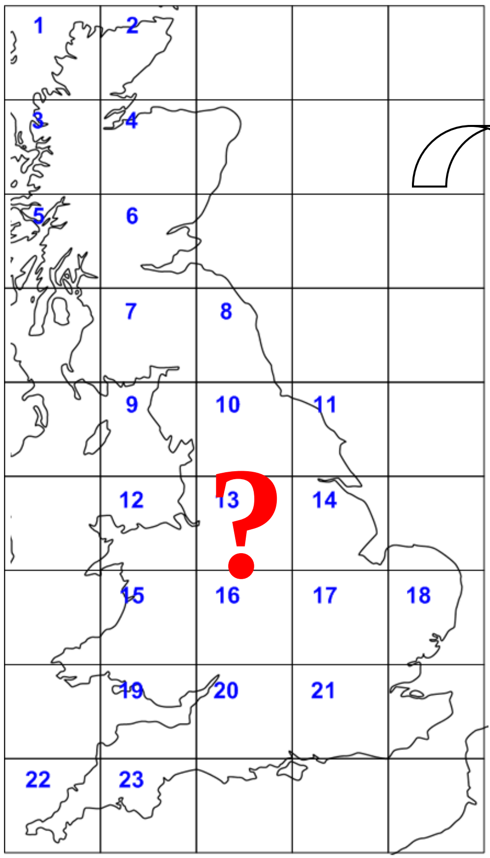
Develop a framework for the design of infrastructures for producing and delivering H_2

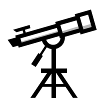
- **Cover the entire supply chain (holistic view of the system)**
- **Include environmental concerns along with traditional economic criteria**
- **Develop an efficient solution method**

Basis: case study by A. Almansoori and N. Shah (2006) in UK

Problem statement

Design of SCs for hydrogen production





Production

- Steam methane reforming
- Coal gasification
- Biomass gasification

Transportation

- Liquid hydrogen (LH) tanker truck
- Liquid hydrogen (LH) railway tank car
- Compressed-gasous hydrogen (CH) tube trailer
- Compressed-gaseous hydrogen (CH) railway tube car

Storage

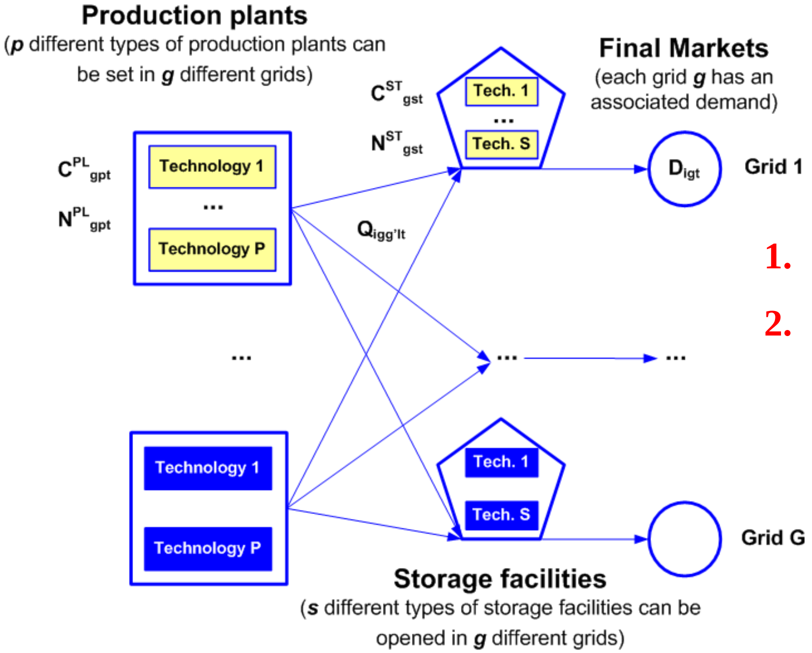
- Liquid hydrogen (LH) storage
- Compressed gas (CH) storage

- **Given are:**
  - ✓ **Demand of hydrogen**
  - ✓ **Investment and operating costs**
  - ✓ **Available technologies and potential locations (i.e., grids)**
  - ✓ **GHG emissions associated with the SC operation**

- **The task is to determine the optimal SC configuration**

- **In order to minimize cost and environmental impact**

Bi-criterion MILP Model



1. Postulate a superstructure with all possible alternatives
2. Build an MILP model with:
   - Economic and Environmental objective functions

Min Cost

Min Environmental impact

s.t. Mass balances (defined for every grid)

Capacity constraints (production and storage)

Capacity constraints (transportation)

0-1 vars choices, cont vars flows

Environmental aspects based on LCA (Eco-Indicator 99)

Life Cycle Analysis-LCA

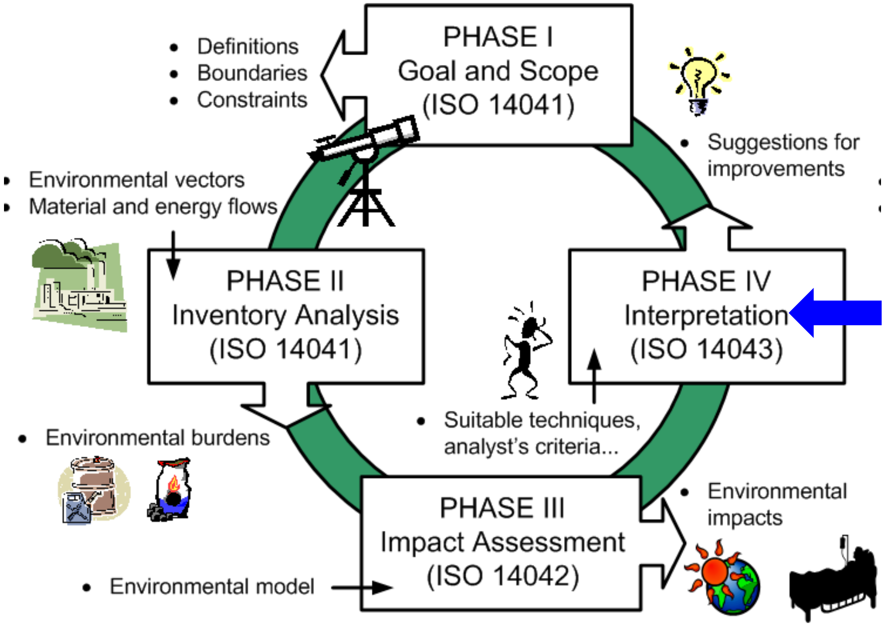
(ISO 14040 series on LCA)

→ **Objective strategy to evaluate the environmental loads associated with a product, process or activity**

by quantifying energy and materials used and waste released

→ **to evaluate opportunities to do improvements**

It includes the ENTIRE LIFE CYCLE of the product

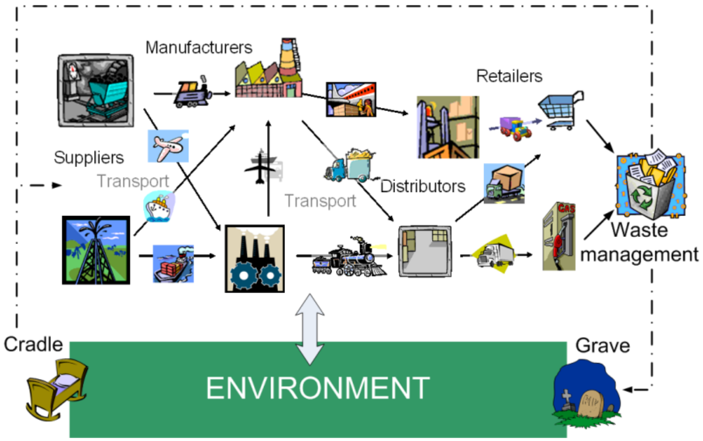


Combine LCA with optimization tools

(Azapagic et al., 1999, Mele et al., 2005, Hugo and Pistikopoulos, 2005)

Environmental damage assessment: Global warming

1. **Calculate the GHG emissions (Life Cycle Inventory: analysis from the cradle to the grave)**



$$LCI_b = \sum_i \sum_g \sum_p \sum_t PR_{igpt}(\omega_{bp}^{PR} + \omega_{bi}^{ST}) + \sum_i \sum_g \sum_{g' \neq g} \sum_{l \in LI(i)} \sum_t Q_{igg'lt}\omega_b^{TR} \quad \forall b$$

Storage (compression of hydrogen)

Production (raw materials, energy consumption and direct emissions)

Transportation tasks

2. **Translate emissions into damage (damage to human health caused by climate change)**

- **Human health:** **DALYs (Disability Adjusted Life Years)**

$$DAM = \sum_b \upsilon_b LCI_b$$

Damage factors translate life cycle inventory into impact

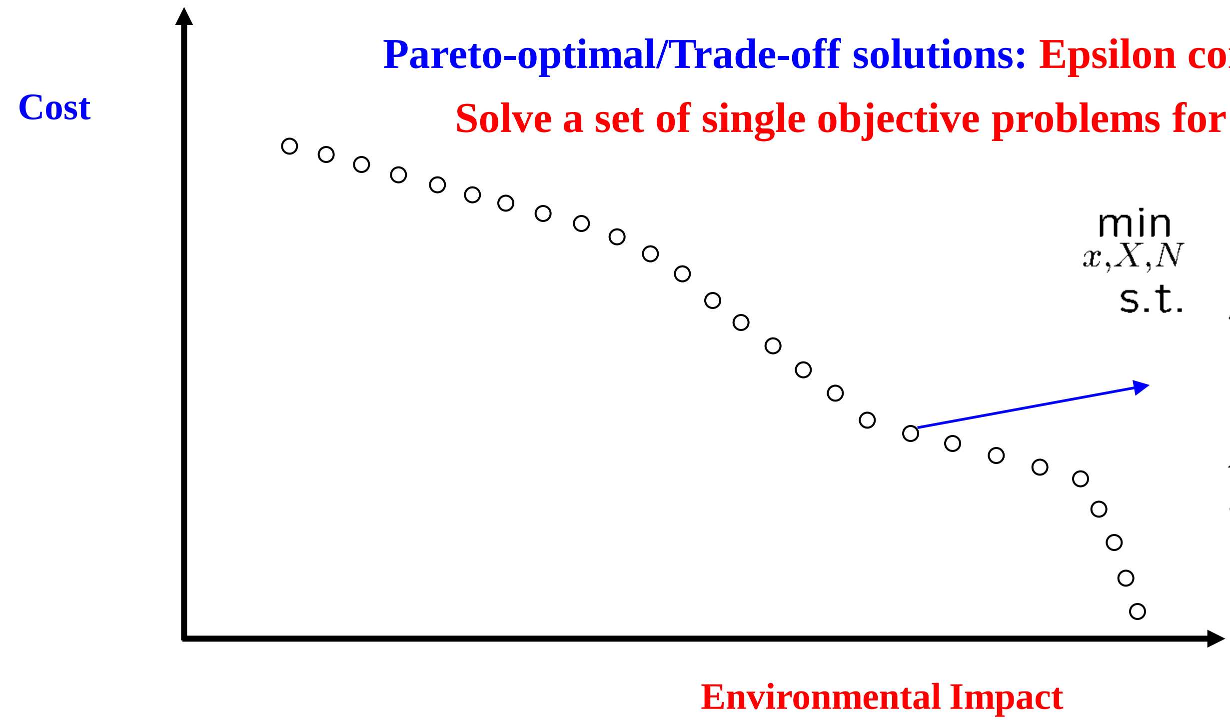
Solution strategy: Epsilon constraint

Bi-criterion MILP with economic and environmental concerns

$$
\begin{aligned}
\min_{x,X,N} \quad & (TDC(x,X,N), DAM(x,X,N)) \\
\text{s.t.} \quad & g(x,X,N) \leq 0 \\
& h(x,X,N) = 0 \\
& x \in \mathbb{R}, X \in \{0,1\}, N \in \mathbb{N}
\end{aligned}
$$

Pareto-optimal/Trade-off solutions: Epsilon constraint method

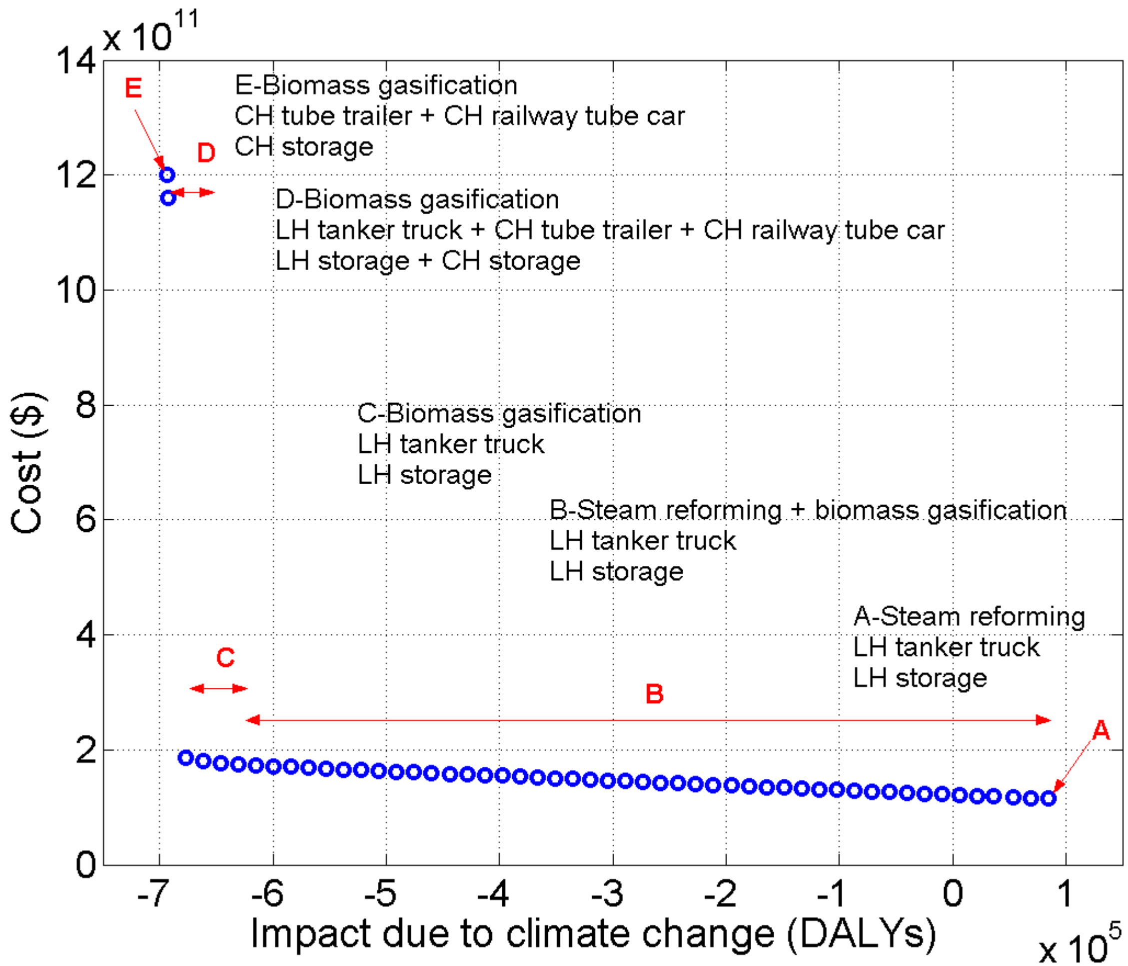
Solve a set of single objective problems for different values of ε



$$
\begin{aligned}
\min_{x,X,N} \quad & (TDC(x,X,N)) \\
\text{s.t.} \quad & g(x,X,N) \leq 0 \\
& h(x,X,N) = 0 \\
& DAM(x,X,N) \leq \epsilon \\
& \underline{\epsilon} \leq \epsilon \leq \overline{\epsilon} \\
& x \in \mathbb{R}, X \in \{0,1\}, N \in \mathbb{N}
\end{aligned}
$$

Pareto set of alternative solutions

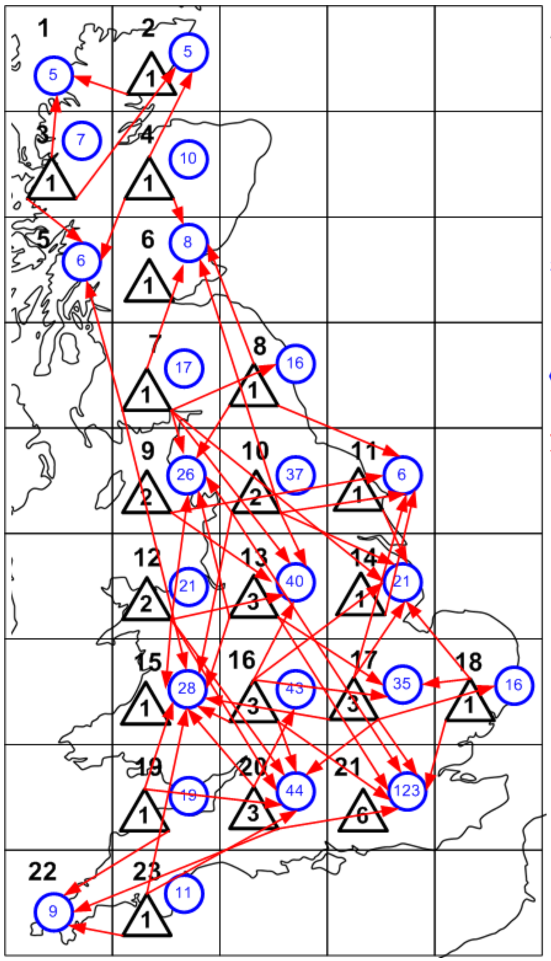
Environmental improvements are achieved through technological and topological changes

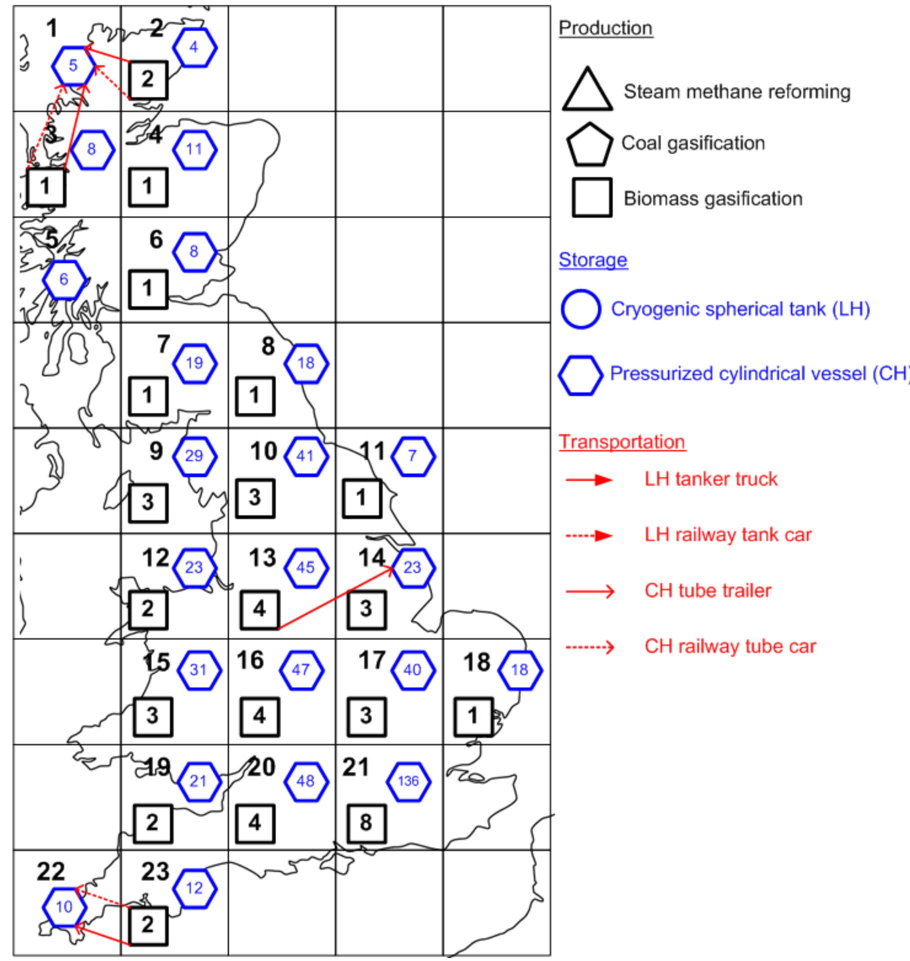


- **Replace steam reforming by biomass**
- **Do not use compressed gaseous hydrogen (too expensive)**

Extreme solutions

Decentralized networks decrease the environmental impact





MINIMUM COST: more <u>centralized</u> network (fewer plants, more transportation)

MINIMUM IMPACT: more <u>decentralized</u> network (more plants, lower transportation emissions)

Conclusions

- Mathematical programming offers a general modeling framework for including sustainability considerations in process synthesis and supply chain optimization problems

- Energy and water optimization yields sustainable designs of biofuel plants: Optimization predicts lower energy and water targets

- Water management optimization in Shale Gas Production has become a problem of great importance

- Supply chain optimization of energy systems can have great impact on sustainability