Mathematical Programming Models and Solution Strategies for the Synthesis of Process Systems

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Sustainability and Energy systems

- Sustainability and energy have recently emerged as key problems

Growing World Energy Demand
Most Energy Growth in Developing Nations

\[ \text{Global Fossil Carbon Emissions} \]

**Sheppard, Socolow (2007)**

**DOE EIA, International Energy Outlook 2006, Figure 8**

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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- **Little or no water scarcity.** Abundant water resources relative to use, with less than 25% of water from rivers withdrawn for human purposes.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 More than 75% of river flows are withdrawn for agriculture, industry, and domestic purposes (accounting for recycling of return flows).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- **Approaching physical water scarcity.** More than 60% of river flows are withdrawn.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 Water resources are abundant relative to water use, with less than 25% of water from rivers withdrawn for human purposes, but malnutrition exists.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.
Design or Synthesis?

Webster Dictionary

Design: The creation of something in the mind.

Oxford Dictionary

Design: a plan or drawing produced to show the look and function or workings of something before it is built or made

Oxford and Webster

Synthesis: the combination of components to form a connected whole

Synthesis: invention of new systems, configurations

Goal: Optimal Design
Major Areas: Process Systems Engineering

Design

Control

Operations

Synthesis Key Problem

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Process Synthesis

The generation of process flowsheet alternatives

(Rudd, Powers, Siirala, 1973)

Given inputs and desired outputs:

\[ \text{Inputs} \rightarrow ? \rightarrow \text{Outputs} \]

*Phenomena to exploit?  
*Equipment to implement?  
*Interconnections?
Subsystems

- Heat exchanger network synthesis
- Separation systems: Distillation systems
- Reactor networks
- Reaction pathways
- Steam and Power plants
- Water networks, mass exchange networks

Basic representations

Process flowsheets

Basic methodologies
Pinch Analysis – Heat exchanger networks

(Hohmann, Linnhoff)

Target min heating/min cooling

Min Heating 600kW

Min Cooling 2250kW

Composite Hot

Composite Cold

HRAT=20K PINCH!! (540-520)

C1

C1+C2

C2

H1

H1 + H2

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Distillation boundaries - Azeotropic Distillation

(Doherity, Perkins)

- Product
- Azeotrope
- Mass Balance
- Distillation Boundary

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Attainable region - Reactor Networks

(Glasser, Hildebrandt)
Subsystems and Process Flowsheets

• Evolutionary Search
  – Start with base case (*Stephanopoulos, Westerberg*)

• Systematic Generation
  – Means-Ends Analysis (*Siirola, Powers*)
  – Hierarchical decomposition (*Douglas*)

• Superstructure Optimization
  – NLP optimization (*Sargent, Gaminibandara*)
  – MINLP, Generalized Disjunctive Programming (*Grossmann*)
Hierarchical decomposition

Douglas (1988)

Batch vs Continuous

Input-Output Level

Recycle System

Separation Synthesis

Heat Recovery
Math Programming Approach to Process Synthesis

1. Develop a superstructure of alternative designs

2. Develop an NLP or (MINLP, GDP) model to select topology and parameters of design

3. Solve NLP or (MINLP, GDP) model to extract optimum design embedded in superstructure

\[
\text{NLP} = \text{Nonlinear Programming} \\
\text{MINLP} = \text{Mixed-integer nonlinear programming} \\
\text{GDP} = \text{Generalized Disjunctive Programming}
\]
Challenges

Postulating superstructure

Capturing all the alternatives
Understanding implications for modeling

Model formulation

Predicting performance: equations
Capturing logic: constraints

Solution algorithm

Exponential behavior due to combinatorics
Overcoming nonconvexities
First step: State and Task Identification in process flowsheet.

STATES:
1- Raw, V, Low P
2- A mixed, V, Low P
3- A mixed, V, Low P to T3
4- A mixed, V, Low P to T4
5- A, V, High P, form T3
6- A, V, High P, form T4
7- A, V, High P, to preheat
8- A, V, High P, High T
9- A, V, to packed reactor
10- A+B, V to mixer T10
11- A, V, to PFR
12- A+B, V to mixer T10
13- A+B, V to cooler
14- A+B, L to flash
15- A+B, Rich in A, V, from purge splitter
16- A, V, low P
17- A+B, L, to distillation
18- B, L, Final Product
19- A, V, High P
20- A+B, L, to distillation
21- A+B, V, waste product

TASKS:
1- Mix recirc A and raw A
2- Split feed mixture
3- Compress in single stage
4- Compress in two stages
5- Mix compressed streams and recycle.
6- Preheat for reaction
7- Split to reactors
8- React A->B in vapor phase in PFR
9- React A->B in vapor phase with catalizer C in packed reactor
10- Mix reactor outlets, Vapor
11- Condense stream
12- Flash A+B: A+B vapor, B liquid
13- Distillate A+B: A liquid, B liquid
14- Compress col. vapor outlet
15- Purge vapor stream
OTOE Assignment for STN

Predetermined Equipment Assignment: One Task One Equipment
Assignment left over for optimization: Variable Task Equipment
State Equipment Network (SEN)

VTE:

Preheat feed to reactor
-or-
Cool reactor outlet
-or-
Vaporize recycle from distillation

React A-->B (liquid phase)
-or-
React A-cat-->B in packed reactor (vapor phase)

Compress Recycle
-or-
Compress Feed
State-Space Superstructure  
Bagajewicz and Manousiouthakis (1992)

Synthesis of mass exchanger networks for batch processes  
Li-Juan Li, Rui-Jie Zhou  
Hong-Guang Dong (2010)

Distribution Network

Operators

- The inlet of each stream is denoted as a splitting node, and the outlet as a mixing node.
- Each mass exchanger is identified by two splitting and mixing nodes, representing the rich and lean sides.
- Each storage tank is expressed as one splitting and mixing node.
Nonlinear Programming (NLP)

\[
\begin{align*}
\text{min } Z &= f(x) \\
\text{s.t. } h(x) &= 0 \\
&\quad g(x) \leq 0 \\
&\quad x \in \mathbb{R}^n
\end{align*}
\]

**LP Codes:**
CPLEX, XPRESS, GUROBI, XA

**NLP Codes:**
BARON Sahinidis et al. (1998)
CONOPT Drud (1998)
Couenne Belotti, Margot (2008)
IPOPT Waechter & Biegler (2006)
MINOS Murtagh, Saunders (1995)
SNOPT Gill, Murray, Saunders (2006)
Mixed-integer Nonlinear Programming (MINLP)

\[
\begin{align*}
\text{min } Z &= f(x, y) \\
\text{s.t. } h(x, y) &= 0 \\
g(x, y) &\leq 0 \\
x &\in \mathbb{R}^n, \ y \in \{0,1\}^m
\end{align*}
\]

**MILP Codes:**
CPLEX, XPRESS, GUROBI, XA

**MINLP Codes:**
DICOPT (GAMS) Duran and Grossmann (1986)
a-ECP Westerlund and Peterssson (1996)
MINOPT Schweiger and Floudas (1998)
BARON Sahinidis et al. (1998)
MINLP-BB (AMPL) Fletcher and Leyffer (1999)
SBB (GAMS) Bussieck (2000)
FilMINT Linderoth and Leyffer (2006)
Couenne Belotti, Margot (2008)
Generalized Disjunctive Programming (GDP)

\[
\min Z = \sum_k c_k + f(x) \\
\text{s.t. } r(x) \leq 0 \\
\bigvee_{j \in J_k} \begin{bmatrix} \gamma_{jk} \\ g_{jk}(x) \leq 0 \end{bmatrix} \quad k \in K \\
\Omega(Y) = \text{true} \\
x \in \mathbb{R}^n, \; c_k \in \mathbb{R}
\]

Boolean Variables

Disjunctions

Logic Propositions

Boolean Variables

Raman, Grossmann (1994)
Methods Generalized Disjunctive Programming

GDP

Logic based methods

Branch and bound
(Lee & Grossmann, 2000)

Decomposition
Outer-Approximation
Generalized Benders
(Turkay & Grossmann, 1997)

Reformulation MINLP
Outer-Approximation
Generalized Benders
Extended Cutting Plane

Convex-hull
Big-M
Cutting plane
(Sawaya & Grossmann, 2004)

Code: LOGMIP (Vecchietti, Grossmann, 2001)
EMP (GAMS)

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Global Optimization Algorithms

Algorithms are based on spatial branch and bound method and rely on rigorous lower bounds to the global optimum

• **Nonconvex NLP/MINLP**
  - αBB \[\text{(Adjiman, Androulakis & Floudas, 1997; 2000)}\]
  - BARON (Branch and Reduce)\[\text{(Ryoo & Sahinidis, 1995, Tawarmalani and Sahinidis (2002))}\]
  - OA for nonconvex MINLP \[\text{(Kesavan, Allgor, Gatzke, Barton, 2004)}\]
  - Branch and Contract \[\text{(Zamora & Grossmann, 1999)}\]

• **Nonconvex GDP**
  - Two-level Branch and Bound \[\text{(Lee & Grossmann, 2001)}\]
  - Strengthening basic steps \[\text{(Ruiz, Grossmann, 2010)}\]
Types of Models

Aggregated models

*High level representations => synthesis problem greatly simplified*

Transshipment model HENS/MENS *(Papoulias, Grossmann, 1983; El-Halwagi, Maniousiouthakis, 1989)*

Distillation Sequences *(Papalexandri, Pistikopoulos, 1996; Caballero, Grossmann, 1999)*

Reactor networks *(Balakrishna, Biegler, 1992; Kravanja, Bedenik, Pahor, 2003)*

Short cut models

*Detailed superstructures with cost optimization but simple performance models*

HENS: *(Yee at al., 1990; Ciric and Floudas, 1991)*

Distillation sequences: *(Aggrawal, and Floudas, 1990; Yeomans and Grossmann, 1998)*

Process flowsheets: *(Kocis and Grossmann, 1989; Türkay and Grossmann, 1996; Lee et al, 2003)*

Rigorous models

*Detailed superstructures with rigorous and complex models*


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Aggregate Model: Transshipment Model for Heat Flows

Unknowns:

a) Utility loads
\[ Q_{\text{Fuel}}, Q_{\text{HP}}, Q_{\text{LP}}, Q_{\text{CW}} \]

b) Heat residuals:
\[ R_1, \ldots R_5 \]
LP transshipment model

Known parameters:  \( Q_{ik}^H, Q_{jk}^C \) heat contents of hot stream \( i \) and cold stream \( j \) in interval \( k \)
\[ c_m, c_n \] unit costs of hot utility \( m \) and cold utility \( n \)

Variables:  \( Q_m^S, Q_n^W \) heat loads of hot utility \( m \) and cold utility \( n \)
\( R_k \) heat residual exiting interval \( k \)

**Linear Program**

\[
\text{min } C = \sum_{m \in S} c_m Q_m^S + \sum_{n \in W} c_n Q_n^W
\]

\[
\text{st } R_k - R_{k-1} - \sum_{m \in S_k} Q_m^S + \sum_{n \in W_k} Q_n^W = \sum_{i \in H_k} Q_{ik}^H - \sum_{j \in C_k} Q_{jk}^C
\]

\[
R_k \geq 0, Q_m^S \geq 0, Q_n^W \geq 0
\]

\[
R_1 = R_K = 0
\]
### Example: 2 hot/2 cold

<table>
<thead>
<tr>
<th>Fcp (MW/C)</th>
<th>Tin(C)</th>
<th>Tout(C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H1</td>
<td>1</td>
<td>400</td>
</tr>
<tr>
<td>H2</td>
<td>2</td>
<td>340</td>
</tr>
<tr>
<td>C1</td>
<td>1.5</td>
<td>160</td>
</tr>
<tr>
<td>C2</td>
<td>1.3</td>
<td>100</td>
</tr>
</tbody>
</table>

#### Temperature intervals (K)

<table>
<thead>
<tr>
<th>Heat contents (MW)</th>
<th>C1</th>
<th>H1</th>
<th>H2</th>
<th>C1</th>
<th>C2</th>
</tr>
</thead>
<tbody>
<tr>
<td>420</td>
<td></td>
<td>400</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>400</td>
<td></td>
<td>380</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>340</td>
<td></td>
<td>320</td>
<td></td>
<td>60</td>
<td>90</td>
</tr>
<tr>
<td>180</td>
<td>250</td>
<td>160</td>
<td>320</td>
<td>240</td>
<td>117</td>
</tr>
<tr>
<td>120</td>
<td></td>
<td>160</td>
<td>120</td>
<td>60</td>
<td>78</td>
</tr>
<tr>
<td>C2</td>
<td>280</td>
<td>440</td>
<td>360</td>
<td>195</td>
<td></td>
</tr>
</tbody>
</table>

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LP Transshipment:

\[
\begin{align*}
\text{min } Z &= Q_s + Q_w \\
\text{s.t. } & R_1 - Q_s = -30 \\
& R_2 - R_1 = -30 \\
& R_3 - R_2 = 123 \\
& Q_w - R_3 = 102 \\
& Q_s, Q_w, R_1, R_2, R_3 \geq 0
\end{align*}
\]

\[
Q_s = 60 \text{ MW}, \quad Q_w = 225 \text{ MW}, \\
R_1 = 30 \text{ MW}, \quad R_2 = 0, \quad R_3 = 123 \text{ MW} \\
R_2 = 0 \Rightarrow \text{pinch point at 340-320C}
\]
Synthesis of Heat Exchanger Networks
Yee and Grossmann (1990)

Multiple stages with potential heat exchangers $z_{ijk} = 0,1$

Two-stage superstructure

**Parameters**
- TIN = inlet temperature of stream
- TOUT = outlet temperature of stream
- F = heat capacity flow rate
- U = overall heat transfer coefficient
- CCU = unit cost for cold utility
- CHU = unit cost of hot utility
- CF = fixed charge for exchangers
- C = area cost coefficient
- B = exponent for area cost
- NOK = total number of stages
- \( \Omega \) = upper bound for heat exchange
- \( \Gamma \) = upper bound for temperature difference

**Variables**
- \( d_{ij,k} \) = temperature approach for match \((i,j)\) at temperature location \(k\)
- \( d_{cui} \) = temperature approach for the match of hot stream \(i\) and cold utility
- \( d_{thuj} \) = temperature approach for the match of cold stream \(j\) and hot utility
- \( q_{ijk} \) = heat exchanged between hot process stream \(i\) and cold process stream \(j\) in stage \(k\)
- \( q_{cu} \) = heat exchanged between hot stream \(i\) and cold utility
- \( q_{hu} \) = heat exchanged between hot utility and cold stream \(j\)
- \( t_{i,k} \) = temperature of hot stream \(i\) at hot end of stage \(k\)
- \( t_{j,k} \) = temperature of cold stream \(j\) at hot end of stage \(k\)
- \( z_{ijk} \) = binary variable to denote existence of match \((i,j)\) in stage \(k\)
- \( z_{cu} \) = binary variable to denote that cold utility exchanges heat with stream \(i\)
- \( z_{hu} \) = binary variable to denote that hot utility exchanges heat with stream \(j\)
Assumption

Isothermal mixing $\Rightarrow$ linear constraints

\[ t_{ik} \quad z_{ijk=0,1} \quad t_{ik+1} \]

Rigorous if no stream splits

Procedure

1. Solve MINLP assuming isothermal mixing
2. If splitting streams, solve NLP on reduced final configuration

No. stages: max \{no. hot, no. cold\}
Overall heat balance for each stream

\[
(TOUT_j - TIN_j) F_j = \sum_{k \in ST} \sum_{i \in HP} q_{ijk} + qhu_j \quad j \in CP
\]

\[
(TIN_i - TOUT_i) F_i = \sum_{k \in ST} \sum_{j \in CP} q_{ijk} + qcu_i \quad i \in HP
\]

Heat balance at each stage

\[
(t_{i,k} - t_{i,k+1}) F_i = \sum_{j \in CP} q_{ijk} \quad i \in HP, k \in ST
\]

\[
(t_{j,k} - t_{j,k+1}) F_j = \sum_{j \in HP} q_{ijk} \quad j \in CP, k \in ST
\]

Feasibility of temperatures

\[
t_{i,k} \geq t_{i,k+1} \quad k \in ST, \; i \in HP
\]

\[
t_{j,k} \geq t_{j,k+1} \quad k \in ST, \; j \in CP
\]

\[
TOUTi \geq t_{i,NOK+1} \quad i \in HP
\]

\[
TOUTj \geq t_{j,1} \quad j \in CP
\]

Hot and cold utility load

\[
(ti_{NOK+1} - TOUTi) F_i = qcu_i \quad i \in HP
\]

\[
(TOUTj - t_{j,1}) F_j = qhu_j \quad j \in CP
\]
Logical constraints

\[ q_{ijk} - \Omega z_{ijk} \leq 0 \quad i \in \text{HP}, \ j \in \text{CP}, \ k \in \text{ST} \]
\[ q_{cui} - \Omega z_{cui} \leq 0 \quad i \in \text{HP} \]
\[ q_{huj} - \Omega z_{huj} \leq 0 \quad j \in \text{CP} \]
\[ z_{ijk}, z_{cui}, z_{huj} = 0, 1 \]

Calculation of approach temperatures

\[ d_{t,ijk} \leq t_{i,k} - t_{j,k} + \Gamma (1 - z_{ijk}) \quad k \in \text{ST}, \ i \in \text{HP}, \ j \in \text{CP} \]
\[ d_{t,ijk} + 1 \leq t_{i,k+1} - t_{j,k+1} + \Gamma (1 - z_{ijk}) \quad k \in \text{ST}, \ i \in \text{HP}, \ j \in \text{CP} \]
\[ d_{t,cui} \leq t_{i,NOK+1} - T_{\text{OUTCU}} + \Gamma (1 - z_{cui}) \quad i \in \text{HP} \]
\[ d_{t,hui} \leq T_{\text{OUTHU}} - t_{j,1} + \Gamma (1 - z_{huj}) \quad j \in \text{CP} \]
\[ d_{t,ijk} \geq \text{EMAT} \]

Objective function

Chen approximation (1987)

\[ \text{LMTD} \approx \left[ \frac{(dt_1 \times dt_2) \times (dt_1 + dt_2)}{2} \right]^{1/3} \]

\[ \min \ Z = \sum_{i \in \text{HP}} CCU_{q_{cui}} + \sum_{j \in \text{CP}} CHU_{q_{huj}} \]
\[ + \sum_{i \in \text{HP}} \sum_{j \in \text{CP}} \sum_{k \in \text{ST}} CF_{ij} z_{ijk} + \sum_{i \in \text{HP}} CF_{i,CU} z_{cui} + \sum_{j \in \text{CP}} CF_{i,HU} z_{huj} \]
\[ + \sum_{i \in \text{HP}} \sum_{j \in \text{CP}} \sum_{k \in \text{ST}} C_{ij} q_{ijk} \left[ \frac{(dt_{ijk})(dt_{ijk+1})}{2} \right]^{1/3} + \ldots \text{etc.} \]

SYNHEAT: http://newton.cheme.cmu.edu/interfaces
**PROCESS STREAMS**

**HOT:**
TIN.FX('1') = 480.00;
TOUT.FX('1') = 340.00;
FCI('1') = 1.50;
CFI('1') = 1.00;

TIN.FX('2') = 420.00;
TOUT.FX('2') = 330.00;
FCI('2') = 2.00;
CFI('2') = 1.00;

**COLD:**
TJJN.FX('1') = 320.00;
TJOUT.FX('1') = 410.00;
FCJ('1') = 1.00;
CFJ('1') = 1.00;

TJJN.FX('2') = 350.00;
TJOUT.FX('2') = 460.00;
FCJ('2') = 2.00;
CFJ('2') = 1.00;

TMAPP = 10.00;

**UTILITIES**

CFHU = 1.00;
THUIN = 500.00;
THUOUT = 500.00;
CFCU = 1.00;
TCUIN = 300.00;
TCUOUT = 300.00;

**COSTS**

**UTILITIES**
HUCOST = 80.00;
CUCOST = 20.00;

UNITC = 1000.00;
ACOEFF = 20.00;
HUCOEFF = 20.00;
CUCOEFF = 20.00;
Total Network Cost ($/yr) = 8962.60
Extension to isothermal streams in the MINLP Model


Hot streams

- **a)** Sensible heat
  
  \[ Q_i = F \rho_i \left( T_{\text{IN}_i} - T_{\text{OUT}_i} \right) \]

- **b)** Isothermal
  
  \[ Q_i = F \lambda_i^{\text{cond}} \]

- **c)** Sensible and latent heat
  
  \[ Q_i = F \rho_i^{\text{sup}} \left( T_{\text{IN}_i} - T_i^{\text{cond}} \right) + F \lambda_i^{\text{cond}} + F \rho_i^{\text{sub}} \left( T_i^{\text{cond}} - T_{\text{OUT}_i} \right) \]

Cold streams

- **d)** Sensible heat
  
  \[ Q_j = F \rho_j \left( T_{\text{OUT}_j} - T_{\text{IN}_j} \right) \]

- **e)** Isothermal
  
  \[ Q_j = F \lambda_j^{\text{evap}} \]

- **f)** Sensible and latent heat
  
  \[ Q_j = F \rho_j^{\text{sup}} \left( T_{\text{OUT}_j} - T_j^{\text{evap}} \right) + F \lambda_j^{\text{evap}} + F \rho_j^{\text{sub}} \left( T_j^{\text{evap}} - T_{\text{IN}_j} \right) \]

Different cases modeled with disjunctions
Example of disjunctive constraint

• Feasibility of Latent Heat Exchange

Outlet temperature for hot stream

\[
\begin{align*}
Y_{i,k}^1 & \geq t_{i,k+1} - T_i^{\text{cond}} + \delta \\
q_{i,k}^\wedge & = 0 \\
& \lor \\
\neg Y_{i,k}^1 & \leq t_{i,k+1} - T_i^{\text{cond}} \\
q_{i,k}^\wedge & \geq 0
\end{align*}
\]

Example of disjunctive constraint
Superstructure for Utility Plants

Ref: Bruno et al. (1998)
MINLP Model for Utility section

Min Material costs (syngas, cooling water, demineralized water; IGCC) (energy requirement like heating and electricity are met internally)

s. t.

Rigorous material and energy balances

Rating / Performance equations for equipments

Logic constraints
- Electricity demand met by gas turbine, HP steam turbine or both
- Mechanical demands met either by electricity or by coupling with turbine shaft
  - If mechanical demand is met by turbine, exactly one turbine can be used.
- Each turbine can contribute exactly one demand

STEAM: http://newtoncheme.cmu.edu/interfaces
Numerical Example for Utility Model

**Demands**
- Electricity: 500 MW
- Mechanical Power No 1: 5 MW
- Mechanical Power No 2: 15 MW
- HP Heating: 5 MW
- MP Heating: 20 MW
- LP Heating: 50 MW

**Pressure of Steam Headers**
- HP: 45 bar
- MP: 20 bar
- LP: 7 bar

**Superstructure**
- 62 process streams
- 3 HP turbines (7 modes)
- 2 MP turbines (3 modes)
- 5 Headers (HP, MP, LP, Cond, Vac)
- 1 Gas turbine (compressor, expander)
- 3 Boilers (HP, MP, HRSG)
- 4 Combustors (GT, Boilers)
- 5 Liquid pumps
- 2 Air blowers
- 1 Deaerator

**Non-convex MINLP problem**
- Binary variables: 44
- Continuous variables: 1275
- Constraints: 1309

Modeled and solved using GAMS/DICOPT (Intel Core 2 Duo 2.4 GHz with 2 GB RAM)
Optimal Solution for Numerical Example

Operating cost = $307.27 Million/yr
Conventional System

Raw Water → Raw Water Treatment → Freshwater → Water-using unit 1 → Water-using unit 2 → Water-using unit 3 → Wastewater

Raw Water → Raw Water Treatment → Freshwater → Water-using unit 1 → Water-using unit 2 → Water-using unit 3 → Wastewater

Boiler Feedwater treatment → Boiler → Steam → Steam System

Boiler Blowdown → Water Loss by Evaporation → Cooling Tower Blowdown

Cooling Tower Blowdown → Other Uses (Housekeeping) → Wastewater Treatment → Discharge

Storm Water
Given is:
- a set of single/multiple water sources with/without contaminants,
- a set of water-using, water pre-treatment, and wastewater treatment operations, sinks and sources of water

Synthesize an integrated process water network
- interconnection of process and treatment units (reuse, recycle)
- the flow rates and contaminants concentration of each stream
- minimum total annual cost of water network

Synthesis Integrated Process Water Networks
- Pinch analysis and mathematical programming models
- Reviews in Bagajewicz (2000), Jeżowski (2008), Bagajewicz and Faria (2009), and Foo (2009).

Approach: Global NLP or MINLP superstructure optimization model
Superstructure for water networks for water reuse, recycle, treatment, and with sinks/sources water

Ahmetovic, Grossmann (2010)

Main features:
- Multiple feeds
- Source/Sink units
- Local recycles
- All possible interconnections
- Fixed and variable flows through process units
Industrial wastewater requires complex treatment networks

Sequential treatment has been chosen with 2-4 Best Available Technologies for the removal of each type of pollutant

Galan, Grossmann (2011)
Superstructure for industrial wastewater treatment

- Solid BATs
- HM. BATs
- Inorg. BATs
- Org. BATs
- Biorg. BATs

Wastewater 1
Wastewater 2
Wastewater 3

Sw1
Sw2
Sw3

MbS
MbH
MbI
MbO
MbB

SpS
SpH
SpI
SpO
SpB

MbH
MbI
MbO
MbB

Final wastewater to discharge
Final Mixer

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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
Splitter

\[ FW_s = FIF_s^L + \sum_{p \in PU} FIP_{s,p}^L + \sum_{d \in DU} FID_{s,d}^L + \sum_{t \in TU} FIT_{s,t}^L \quad \forall s \in SW \]

**linear**

\[ FIF_s^L \cdot y_{FIF_s} \leq FIF_s^U \cdot y_{FIF_s} \quad \forall s \in SW \]

\[ FIP_{s,p}^L \cdot y_{FIP_{s,p}} \leq FIP_{s,p}^U \cdot y_{FIP_{s,p}} \quad \forall s \in SW, \forall p \in PU \]

\[ FID_{s,d}^L \cdot y_{FID_{s,d}} \leq FID_{s,d}^U \cdot y_{FID_{s,d}} \quad \forall s \in SW, \forall d \in DU \]

\[ FIT_{s,t}^L \cdot y_{FIT_{s,t}} \leq FIT_{s,t}^U \cdot y_{FIT_{s,t}} \quad \forall s \in SW, \forall t \in TU \]

**0-1 optional**

Mixer

\[ FPU_{p}^{in} = \sum_{r \in SU} FSP_{r,p} + \sum_{t \in TU} FTP_{t,p} + \sum_{s \in SW} FIP_{s,p} + \sum_{p' \in PU, p \neq p', R_{p,p'} = 0} FP_{p',p} + \sum_{p' \in PU, R_{p,p'} = 1} FP_{p',p}, \quad \forall p \in PU \]

Process unit

\[ FPU_{p}^{in} = FPU_{p}^{out}, \quad \forall p \in PU \]

**linear if**

\[ FPU_{p,j}^{in} \cdot x_{PU_{p,j}}^{in} + LPU_{p,j} \cdot 10^3 = FPU_{p,j}^{out} \cdot x_{PU_{p,j}}^{out}, \quad \forall p \in PU, \forall j \]

**bilinear if the flow treated as cont. variable**

Carnegie Mellon
Cost function linear in feedwater, concave in treatment unit, linear in operating cost, pipe section fixed charge (0-1)

\[
\min Z = H \cdot \sum_{s \in SW} FW_s \cdot CFW_s + AR \cdot \sum_{t \in TU} IC_t \cdot FTU_t + \sum_{t \in TU} OC_t \cdot FTU_t^{out}
\]
Controlling complexity network

Limit number of 0-1 vars to $N_{\max}$ number “removable” pipes

\[
\begin{align*}
\sum_{s \in SW} \sum_{p \in PU} y_{FIP_{s,p}} &+ \sum_{s \in SW} \sum_{t \in TU} y_{FIT_{s,t}} + \sum_{s \in SW} y_{FIF_{s}} + \sum_{p' \in PU} \sum_{p \in PU} y_{FP_{p',p}} + \sum_{p' \in PU} \sum_{p \in PU} y_{FP_{p',p}} + \sum_{p \in PU} y_{FPO_{p}} \\
+ \sum_{p \in PU} \sum_{t \in TU} y_{FPT_{p,t}} &+ \sum_{t' \in TU} \sum_{t \in TU} y_{FT_{t',t}} + \sum_{t' \in TU} \sum_{t \in TU} y_{FT_{t',t}} + \sum_{t \in TU} y_{FTO_{t}} + \sum_{t \in TU} \sum_{p \in PU} y_{FTP_{t,p}} \\
+ \sum_{s \in SW} \sum_{d \in DU} y_{FID_{s,d}} &+ \sum_{p \in PU} \sum_{d \in DU} y_{FPD_{p,d}} + \sum_{t \in TU} \sum_{d \in DU} y_{FTD_{t,d}} + \sum_{r \in SU} \sum_{d \in DU} y_{FSD_{r,d}} + \sum_{r \in SU} y_{FSO_{r}} \\
+ \sum_{r \in SU} \sum_{t \in TU} y_{FST_{r,t}} &+ \sum_{r \in SU} \sum_{p \in PU} y_{FSP_{r,p}} \leq N_{\max}
\end{align*}
\]

Can develop trade-off curve solving successive MINLPs

Cost

$N_{\max}$
Convexification of Non-convex functions

Convex Envelopes for Bilinear Terms $F^*C$

McCormick (1976)

Under- and over-estimators
(Linear Inequalities)

$F_i^L \leq F_i \leq F_i^U$
$C_j^i_L \leq C_j^i \leq C_j^i_U$

Underestimation of Concave functions

( Secant line )

$F_i^L \leq F_i \leq F_i^U$

Carnegie Mellon
• The cut proposed by Karuppiah and Grossmann (2006) is incorporated to
  significantly improve the strength of the lower bound for the global optimum:
  contaminant flow balances for the overall water network system

\[
\sum_{s \in SW} FW_s \cdot x_{W_{in}}^{s,j} + \sum_{p \in PU} LPU_{p,j} \cdot 10^3 + \sum_{r \in SU} FSU^\text{out}_{r,j} \cdot xSU^\text{out}_{r,j} = \sum_{t \in TU} (1 - \beta_{TU_{t,j}}) \cdot FTU_{t,j} \cdot xTU_{t,j}^\text{in}
\]

\[+ F^\text{out}_{j} \cdot x_{j}^\text{out} + \sum_{d \in DU} FDU^\text{in}_{d,j} \cdot xDU_{d,j}^\text{in} \quad \forall j \]

bilinear terms for the treatment units and final mixing points

Cut is redundant for original problem
Non-redundant for relaxation problem

• Tight bounds on the variables are expressed as general equations
  obtained by physical inspection of the superstructure and using logic specifications

WATER: http://newton.cheme.cmu.edu/interfaces
Example 1

The objective of this example is to:
- solve NLP and MINLP water network problems
- compare results obtained with/without allowed recycle around process units
- illustrate how the complexity of the water networks can be controlled

Data of process units.

<table>
<thead>
<tr>
<th>Unit</th>
<th>Flow rate (t/h)</th>
<th>Discharge load (kg/h) A</th>
<th>B</th>
<th>Maximum inlet concentration (ppm) A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>PU1</td>
<td>40</td>
<td>1</td>
<td>1.5</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>PU2</td>
<td>50</td>
<td>1</td>
<td>1</td>
<td>50</td>
<td>50</td>
</tr>
</tbody>
</table>

Data of treatment units.

<table>
<thead>
<tr>
<th>Unit</th>
<th>% Removal for contaminant A</th>
<th>B</th>
<th>IC (Investment cost coefficient)</th>
<th>OC (Operating cost coefficient)</th>
<th>$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TU1</td>
<td>95</td>
<td>0</td>
<td>16800</td>
<td>1</td>
<td>0.7</td>
</tr>
<tr>
<td>TU2</td>
<td>0</td>
<td>95</td>
<td>12600</td>
<td>0.0067</td>
<td>0.7</td>
</tr>
</tbody>
</table>
Example 1

Superstructure of integrated water network with two process and two treatment units

NLP and MINLP solved to global optimality with BARON
Selected optimality tolerance = 0.0
## Model statistics and computational results for Example 1

<table>
<thead>
<tr>
<th>Continuous variables</th>
<th>Discrete variables</th>
<th>Constraints</th>
<th>CPU time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>55</td>
<td>-</td>
<td>44</td>
<td>&lt; 0.5</td>
</tr>
<tr>
<td>57*</td>
<td>-</td>
<td>44</td>
<td>&lt; 1.0</td>
</tr>
<tr>
<td>75</td>
<td>20</td>
<td>85</td>
<td>&lt; 3.6</td>
</tr>
<tr>
<td>79*</td>
<td>22</td>
<td>89</td>
<td>&lt; 2.5</td>
</tr>
<tr>
<td>77**</td>
<td>20</td>
<td>85</td>
<td>13.2</td>
</tr>
</tbody>
</table>

*Option with local recycles. **Variable flowrates in process units.
Example 1

Case 1 (NLP): Objective function: cost of water, investment cost on treatment units and operating cost for treatment units

<table>
<thead>
<tr>
<th></th>
<th>Without recycle</th>
<th>With recycle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freshwater cost</td>
<td>$320000</td>
<td>$320000</td>
</tr>
<tr>
<td>Investment cost on treatment units</td>
<td>$37440</td>
<td>$33585.3</td>
</tr>
<tr>
<td>Operating costs for treatment units</td>
<td>$238723.6</td>
<td>$230431.6</td>
</tr>
<tr>
<td>Total cost</td>
<td>$596163.6</td>
<td>$584016.9</td>
</tr>
</tbody>
</table>

Case 2 (MINLP): Objective function: cost of water, investment cost on treatment units, operating cost for treatment units, investment cost on pipes, operating cost for pumping water through pipes

<table>
<thead>
<tr>
<th></th>
<th>Without recycle</th>
<th>With recycle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freshwater cost</td>
<td>$320000</td>
<td>$320000</td>
</tr>
<tr>
<td>Investment cost on pipes</td>
<td>$540.69</td>
<td>$546.3</td>
</tr>
<tr>
<td>Operating cost for pumping water</td>
<td>$10056.26</td>
<td>$9427.84</td>
</tr>
<tr>
<td>Investment cost on treatment units</td>
<td>$37440.01</td>
<td>$33585.32</td>
</tr>
<tr>
<td>Operating costs for treatment units</td>
<td>$238723.59</td>
<td>$230431.64</td>
</tr>
<tr>
<td>Total cost</td>
<td>$606760.55</td>
<td>$593991.1</td>
</tr>
</tbody>
</table>

2% saving with recycle
8 “removable connections”

Optimal solution for the NLP and MINLP problem **without local recycle**

9 “removable connections”

Optimal solution for the NLP and MINLP problem **with local recycle**
Pareto-optimal solutions for minimum cost and minimum number of removable connections
## Example 2

**Objective of this example:** show that proposed model can be used to establish trade-off complexity vs cost of water network

### Data for process units

<table>
<thead>
<tr>
<th>Unit</th>
<th>Flow rate (t/h)</th>
<th>Discharge load (kg/h)</th>
<th>Maximum inlet concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>A</td>
<td>B</td>
</tr>
<tr>
<td>PU 1</td>
<td>40</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>PU 2</td>
<td>50</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>PU 3</td>
<td>60</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>PU 4</td>
<td>70</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>PU 5</td>
<td>80</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

### Data for treatment units

<table>
<thead>
<tr>
<th>Unit</th>
<th>Removal ratio (%)</th>
<th>IC (Investment cost coefficient)</th>
<th>OC (Operating cost coefficient)</th>
<th>$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>B</td>
<td>C</td>
<td></td>
</tr>
<tr>
<td>TU 1</td>
<td>95</td>
<td>0</td>
<td>0</td>
<td>16800</td>
</tr>
<tr>
<td>TU 2</td>
<td>0</td>
<td>0</td>
<td>95</td>
<td>9500</td>
</tr>
<tr>
<td>TU 3</td>
<td>0</td>
<td>95</td>
<td>0</td>
<td>12600</td>
</tr>
</tbody>
</table>
Superstructure of the integrated water network

MINLP: 72 0-1 vars, 233 cont var, 251 constr
optcr=0.01 197.5 CPUsec
Example 2

Cost of water network for different number of removable piping connections

Note: reduction 7 pipe segments => 28 % increase in cost
Optimal design of the simplified water network with 13 removable connections
Large scale water network problem
4 feeds, 6 process units, 4 treatment units, 3 contaminants

Optimal Freshwater Consumption
40 t/h
vs
390 t/h
conventional

NLP: 232 variables, 121 constraints  BARON: 2 secs
Simultaneous heat and water flowsheet optimization

Flowsheets with recycle

Advantage Simultaneous vs Sequential
Leads to total lower cost and higher overall conversion
Strategy for simultaneous optimization

*Duran, Grossmann (1986)  Yang, Grossmann (2011)*
Target Minimum Utility Cost
Pinch Location Method

Basic idea: Assume pinch occurs at every inlet and determine maximum heating

(a) Pinch candidate H1

(b) Pinch candidate H2

(c) Pinch candidate C1

(d) Pinch candidate C2
LP targeting model (parametric in flows, temperatures)

\[
\begin{align*}
    &\text{min } C = f(x) + c_S Q_S + c_W Q_W \\
    &\text{s.t. } h(x) = 0 \\
    &g(x) \leq 0
\end{align*}
\]

Min obj plus cost heating and cooling

Heat balance above pinch point for heating utility

\[
Q_S \geq \sum_{i=1}^{n_c} f_i \left[ \max \left\{ 0, t_j^{\text{out}} - (T^p - \Delta T_{\text{min}}) \right\} - \max \left\{ 0, t_j^{\text{in}} - (T^p - \Delta T_{\text{min}}) \right\} \right]
\]

- \sum_{i=1}^{n_H} F_i \left[ \max \left\{ 0, T_i^{\text{in}} - T^p \right\} - \max \left\{ 0, T_i^{\text{out}} - T^p \right\} \right]

Total heat balance for cooling utility

\[
Q_W = Q_S + \sum_{i=1}^{n_H} F_i (T_i^{\text{in}} - T_i^{\text{out}}) - \sum_{j=1}^{n_c} f_j (t_j^{\text{out}} - t_j^{\text{in}})
\]

\[
\begin{align*}
    Q_S, Q_W \geq 0, & \quad F_i \geq 0 \quad i = 1... n_H, \quad F_j \geq 0 \quad j = 1... n_C \quad x \in R^n
\end{align*}
\]

where \( T_p, p \in P \) Pinch Candidate

Heat integration constraints
Example Simultaneous Optimization and Heat Integration

Optimize operating conditions of flowsheet while integrating hot and cold streams to minimize utility cost

*H1  superheat to dew point
H2  dew point to supercool
**ECONOMIC**

**Expenses (x 10^6 $ / yr):**

<table>
<thead>
<tr>
<th>Item</th>
<th>Simultaneous</th>
<th>Sequential</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feedstock</td>
<td>22.6717</td>
<td>26.4166</td>
</tr>
<tr>
<td>Capital investment</td>
<td>3.7596</td>
<td>3.9108</td>
</tr>
<tr>
<td>Electricity compress</td>
<td>2.3774</td>
<td>2.4871</td>
</tr>
<tr>
<td>Heating utility</td>
<td>2.8244</td>
<td>14.4586</td>
</tr>
<tr>
<td>Cooling utility</td>
<td>0.7900</td>
<td>0.7247</td>
</tr>
</tbody>
</table>

**Earnings (x 10^6 $ / yr):**

<table>
<thead>
<tr>
<th>Item</th>
<th>Simultaneous</th>
<th>Sequential</th>
</tr>
</thead>
<tbody>
<tr>
<td>Product</td>
<td>41.5300</td>
<td>41.5300</td>
</tr>
<tr>
<td>Purge</td>
<td>4.5169</td>
<td>6.8242</td>
</tr>
<tr>
<td>Generated steam</td>
<td>5.6407</td>
<td>9.7441</td>
</tr>
</tbody>
</table>

**Annual Profit**

- **Simultaneous:** 19.2645 (90% HIGHER!)
- **Sequential:** 10.1005

---

**TECHNICAL**

**Overall conversion A**

<table>
<thead>
<tr>
<th>Item</th>
<th>Simultaneous</th>
<th>Sequential</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure reactor</td>
<td>12.10</td>
<td>13.87 [atm]</td>
</tr>
<tr>
<td>Conversion per pass</td>
<td>30.43</td>
<td>37.53 [%]</td>
</tr>
<tr>
<td>Temp. inlet reactor</td>
<td>450.00</td>
<td>450.00 [°K]</td>
</tr>
<tr>
<td>Temp. outlet reactor</td>
<td>502.65</td>
<td>450.00 [°K]</td>
</tr>
<tr>
<td>Steam generated</td>
<td>10119.12</td>
<td>17479.60 [kW]</td>
</tr>
<tr>
<td>Pressure in flash</td>
<td>9.10</td>
<td>10.87 [atm]</td>
</tr>
<tr>
<td>Temperature flash</td>
<td>320.00</td>
<td>339.88 [°K]</td>
</tr>
<tr>
<td>Purge rate</td>
<td>9.66</td>
<td>19.66 [%]</td>
</tr>
<tr>
<td>Power compressors</td>
<td>11353.60</td>
<td>11877.44 [kW]</td>
</tr>
<tr>
<td>Heating utility</td>
<td>1684.27</td>
<td>8622.04 [kW]</td>
</tr>
<tr>
<td>Cooling utility</td>
<td>10632.04</td>
<td>9752.77 [kW]</td>
</tr>
<tr>
<td>Total heat exchanged</td>
<td>31962.20</td>
<td>28720.61 [kW]</td>
</tr>
</tbody>
</table>

**Higher profit**

**Higher conversion**
Simultaneous optimization
Lower heating

Sequential optimization
Higher heating
LP Targeting model for minimum freshwater consumption

Yang, Grossmann (2011)

Assumes only process units (reuse, recycle)

\[
\begin{align*}
\min \quad & Z = F_{fw} \\
\text{s.t.} \quad & F^k = \sum_{i \in m_{in}} F^i \quad \forall m \in MU, k \in m_{out} \\
& F_k C^k_j \geq \sum_{i \in m_{in}} F_i C^i_j \quad \forall j, \forall m \in MU, k \in m_{out} \\
& F^k = \sum_{i \in s_{out}} F^i \quad \forall s \in SU, k \in s_{in} \\
& C^k_j = C^i_j \quad \forall j, \forall s \in SU, \forall i \in s_{out}, k \in s_{in} \\
& F^k = P^p_{in} \quad \forall p \in PU, k \in p_{out} \\
& F^i = P^p_{out} \quad \forall p \in PU, i \in p_{in} \\
& (F^i - \text{Loss}^p)C^i_j + L^p_j = (F^k - \text{Gain}^p)C^k_j \\
& \forall j, \forall p \in PU, i \in p_{in}, k \in p_{out}
\end{align*}
\]

Mixer mass balances

Splitters mass balances

Process unit mass balances
Simultaneous optimization, heat and water integration

\[ \begin{align*}
\min \quad & \phi = F(x, u, v) + \sum_{i \in HU} c_H^i Q_H^i + \sum_{j \in CU} c_C^j Q_C^j + c_{fw} FW \\
\text{s.t.} \quad & h(x, u, v) = 0 \\
& g^P(x, u, v) \leq 0 \\
& g^{HEN}(u, Q_H, Q_C) \leq 0 \\
& g^{WN}(v, FW) \leq 0 \\
& x \in X, \quad u \in U, \quad v \in V
\end{align*} \]

- **Utility cost**
- **Freshwater cost**

- **Process flowsheet constraints**
- **Heat targeting constraints**
- **Water targeting constraints**

Design parameters: $P, V, T, F$

Heat integration parameters: $F_i, T_{i, \text{in}}, T_{i, \text{out}}$

Water integration parameters:
Simultaneous optimization, heat and water integration

methanol synthesis from syngas

+ cooling system
+ steam system

Freshwater requirement

Carnegie Mellon
### Sequential vs simultaneous comparison

<table>
<thead>
<tr>
<th></th>
<th>Sequential</th>
<th>Simultaneous</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Profit (1000 $/yr)</strong></td>
<td>62,695</td>
<td>73,416</td>
</tr>
<tr>
<td><strong>Investment cost (1000 $)</strong></td>
<td>1,891</td>
<td>1,174</td>
</tr>
<tr>
<td><strong>Operating costs and parameters</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>electricity (KW)</td>
<td>6.59</td>
<td>1.84</td>
</tr>
<tr>
<td>freshwater (kmol/s)</td>
<td>202.4</td>
<td>162.5</td>
</tr>
<tr>
<td>heating utility (10^9 KJ/yr)</td>
<td>0.29</td>
<td>0</td>
</tr>
<tr>
<td>cooling utility (10^9 KJ/yr)</td>
<td>67.3</td>
<td>72.7</td>
</tr>
<tr>
<td>Steam generated (10^9 kJ/yr)</td>
<td>2448</td>
<td>1965</td>
</tr>
<tr>
<td>overall conversion</td>
<td>0.23</td>
<td>0.29</td>
</tr>
<tr>
<td><strong>Material flowrate (10^6 kmol/yr)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>feedstock</td>
<td>48.04</td>
<td>37.13</td>
</tr>
<tr>
<td>product</td>
<td>10.89</td>
<td>10.89</td>
</tr>
<tr>
<td>byproduct</td>
<td>9.95</td>
<td>4.41</td>
</tr>
</tbody>
</table>

17% improvement in profit

* Solved with BARON
Synthesis of Distillation Sequences

Example of MILP model for 4 component mixture

Separate mixture of A(lightest), B, C, D (heaviest) into pure components using sharp separators

Andrecovich, Westerberg (1985)

F_i flows, y_i existence columns

Network superstructure for 4 component example.
Data for example problem

a) Initial field

\[ F_{TOT} = 1000 \text{ kgmol/hr} \]

Composition (mole fraction)

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.15</td>
<td>0.3</td>
<td>0.35</td>
<td>0.2</td>
</tr>
</tbody>
</table>

b) Economic data and heat duty coefficients

<table>
<thead>
<tr>
<th>k ( K_k )</th>
<th>Separator</th>
<th>( \alpha_k ), fixed,</th>
<th>( \beta_k ), variable</th>
<th>Heat duty coefficients,</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>A/BCD</td>
<td>145</td>
<td>0.42</td>
<td>0.028</td>
</tr>
<tr>
<td>2</td>
<td>AB/CD</td>
<td>52</td>
<td>0.12</td>
<td>0.042</td>
</tr>
<tr>
<td>3</td>
<td>ABC/D</td>
<td>76</td>
<td>0.25</td>
<td>0.054</td>
</tr>
<tr>
<td>4</td>
<td>A/BC</td>
<td>25</td>
<td>0.78</td>
<td>0.024</td>
</tr>
<tr>
<td>5</td>
<td>AB/C</td>
<td>44</td>
<td>0.11</td>
<td>0.039</td>
</tr>
<tr>
<td>6</td>
<td>B/CD</td>
<td>38</td>
<td>0.14</td>
<td>0.040</td>
</tr>
<tr>
<td>7</td>
<td>BC/D</td>
<td>66</td>
<td>0.21</td>
<td>0.047</td>
</tr>
<tr>
<td>8</td>
<td>A/B</td>
<td>112</td>
<td>0.39</td>
<td>0.022</td>
</tr>
<tr>
<td>9</td>
<td>B/C</td>
<td>37</td>
<td>0.08</td>
<td>0.036</td>
</tr>
<tr>
<td>10</td>
<td>C/D</td>
<td>58</td>
<td>0.19</td>
<td>0.044</td>
</tr>
</tbody>
</table>

Cost of utilities:

Cooling water \( C_C = 1.3 \times 10^3 \text{$/hr/10^6$Jyr} \)

Steam \( C_H = 34 \times 10^3 \text{$/hr/10^6$Jyr} \)
Assume perfect recoveries

Split fractions in superstructure (using initial compositions)

\[ \xi_1^A = 0.15 \]
\[ \xi_1^{BCD} = 0.85 \]
\[ \xi_2^{AB} = 0.45 \]
\[ \xi_2^{CD} = 0.55 \]
\[ \xi_3^{ABC} = 0.8 \]
\[ \xi_3^D = 0.2 \]
\[ \xi_4^B = 0.353 \]
\[ \xi_4^{CD} = 0.647 \]
\[ \xi_5^{BC} = 0.765 \]
\[ \xi_5^D = 0.235 \]
MILP model

Initial node in network

\[ F_1 + F_2 + F_3 = 1000 \]  \hspace{1cm} (1)

For the remaining nodes in the network, mass balances for each 
intermediate product. Based on the recovery fractions, the mass balance
for each intermediate product is as follows:

a) Intermediate (BCD) which is produced in column 1, and directed
to columns 4 and 5,

\[ F_4 + F_5 - 0.85 F_1 = 0 \]  \hspace{1cm} (2)

b) Intermediate (ABC) which is produced in column 3, and directed
to columns 6 and 7,

\[ F_6 + F_7 - 0.8 F_3 = 0 \]  \hspace{1cm} (3)

c) Intermediate (AB) which is produced in columns 2 and 7, and
directed to column 10,

\[ F_{10} - 0.45 F_2 - 0.563 F_7 = 0 \]  \hspace{1cm} (4)

d) Intermediate (BC) which is produced in columns 5 and 6, and
directed to column 9,

\[ F_9 - 0.765 F_5 - 0.812 F_6 = 0 \]  \hspace{1cm} (5)

e) Intermediate (CD) which is produced in columns 2 and 4, and
directed to column 8,

\[ F_8 - 0.55 F_2 - 0.647 F_4 = 0 \]  \hspace{1cm} (6)
Relating flows to the binary variables $y$:

$$F_k - 1000 \cdot y_k \leq 0$$

$$F_k \leq U'y_k = 0,1, \quad k = 1,...,10 \quad (7)$$

Heat duties of condensers and reboliers, continuous variables $Q_k, k = 1, ...10$,

$$Q_k = K_k \cdot F_k, \quad k = 1,...,10 \quad (8)$$

where the parameters $K_k$ are given in Table.

Objective function, minimization of the sum of the costs in the 10 columns.

$$\min \ C = \sum_{k=1}^{10} (\alpha_k y_k + \beta_k F_k) + (34 + 1.3) \sum_{k=1}^{10} Q_k$$

cost coefficients $\alpha_k, \beta_k$, are given in Table.
Optimal separation sequence

Second best solution. Make $y_2 = y_8 = y_{10} = 1$ infeasible

$y_2 + y_8 + y_{10} \leq 2$

Second best sequence
Olefin Separation System \textit{(BP)}

\textit{(Lee, Foral, Logsdon, Grossmann, 2003)}

\textbf{Goal: Synthesize optimal separation system}

\begin{itemize}
  \item \textbf{Input}
    \begin{itemize}
      \item \textbf{Feed}
        \begin{itemize}
          \item Ethane C\textsubscript{2}H\textsubscript{6}
          \item Propane C\textsubscript{3}H\textsubscript{8}
          \item Butane C\textsubscript{4}H\textsubscript{10}
          \item Naphtha C\textsubscript{8}~C\textsubscript{12}
        \end{itemize}
      \end{itemize}
  \item \textbf{RXN System}
    \begin{itemize}
      \item Pyrolysis Furnaces
    \end{itemize}
  \item \textbf{Components}
    \begin{itemize}
      \item \textbf{Mixture}
        \begin{itemize}
          \item Hydrogen H\textsubscript{2}
          \item Fuel gas CH\textsubscript{4}
          \item Acetylene C\textsubscript{2}H\textsubscript{2}
          \item Ethylene C\textsubscript{2}H\textsubscript{4}
          \item Ethane C\textsubscript{2}H\textsubscript{6}
          \item MAPD C\textsubscript{3}H\textsubscript{4}
          \item Propylene C\textsubscript{3}H\textsubscript{6}
          \item Propane C\textsubscript{3}H\textsubscript{8}
          \item C\textsubscript{4} Mixture
          \item C\textsubscript{5} Mixture
          \item C\textsubscript{6+} Mixture
        \end{itemize}
    \end{itemize}
  \item \textbf{Separation}
    \begin{itemize}
      \item \textbf{Separation Tasks}
    \end{itemize}
  \item \textbf{Output}
    \begin{itemize}
      \item Hydrogen H\textsubscript{2}
      \item Fuel gas CH\textsubscript{4}
      \item Ethylene C\textsubscript{2}H\textsubscript{4}
      \item Propylene C\textsubscript{3}H\textsubscript{6}
      \item C\textsubscript{4} Mixture
      \item C\textsubscript{5} Mixture
      \item C\textsubscript{6+} Mixture
    \end{itemize}
  \item \textbf{Recycle}
    \begin{itemize}
      \item Ethane C\textsubscript{2}H\textsubscript{6}
      \item Propane C\textsubscript{3}H\textsubscript{8}
    \end{itemize}
\end{itemize}
Process Superstructure

25 states
53 separation task

Feed
MINLP Model

- GDP reformulated as a MINLP

- Problem Size
  - No. of 0-1 variables = 5,800
  - No. of variables = 24,500
  - No. of constraints = 52,700

- GAMS/DICOPT
  - NLP solver: CONOPT2/ MIP solver: CPLEX
  - CPU time ~ 3 hrs on Pentium III PC

- Verification: ASPENPLUS model
  - Fixed process configuration is simulated/optimized
MINLP optimal solution

Dephlegmator first process
7 separation units

20M$/yr cost saving

1 dephlegmator
1 absorber
4 distillation columns
1 cold box
1 heat exchange

Total cost: 110.82 MM$/yr

Carnegie Mellon
Optimal Feedtray Location

Sargent & Gaminibandara (1976)

NLP Formulation

\[ \text{Min cost} \]
\[ \text{st } \text{MESH eqtns} \]
\[ \sum_{i \in \text{Loc}} f_i = F \]

NLP VMP: Variable-Metric Projection
Optimal Feedtray Location (Cont)

Viswanathan & Grossmann (1990)

MINLP Formulation

\[
\text{Min cost} \\
\text{st } \text{MESH eqtns} \\
\sum_{i \in \text{Loc}} z_i = 1 \\
\sum_{i \in \text{Loc}} f_i = F \\
f_i - F z_i \leq 0 \quad i \in \text{Loc} \\
z_i = 0, 1 \quad i \in \text{Loc}
\]

\text{MINLP DICOPT: AP-Outer Approximation-ER}

Remark: MINLP solves as relaxed NLP!

Feed tray composition tends to match composition of feed
Optimization of Number of Trays

Viswanathan & Grossmann (1993)

Discrete variables: Number of trays, feed tray location.
Continuous variables: reflux ratio, heat loads, exchanger areas, column diameter.

Zero flows- Discontinuities appear, convergence difficulties.
Redundant equations are solved- Increases CPU time.
Optimal Design Columns with Multiple Feeds

Air Products & Chemicals
Separation Methanol - Water with 3 Feeds

Viswanthan & Grossmann (1993)

MINLP model
Virial/UNIQUAC
115 0-1 binary variables
1683 continuous variables
1919 constraints

Solved with DICOPT on a HP 9000/730
(5 major iterations, 45 min)

Optimal solution
Number of trays = 53

Feed location:
Feed 1    Tray 4
Feed 2    Tray 6
Feed 3    Tray 12

700,000 alternatives!
Disjunctive Programming Model

Yeomans & Grossmann (2000)

Permanent trays:
Feed, reboiler, condenser

Conditional trays:
Intermediate trays might be selected or not.

Trays not allowed to “disappear” from column:

VLE mass transfer if selected.

No VLE, trivial mass/energy balance if not selected.

Disjunction

VLE

-OR-

NOT VLE (tray bypass)
Single Column GDP Model

- **Permanent and conditional trays:**
  - MESH equations for condenser, reboiler and feed trays
  - Mass & energy balances for rectification and stripping trays.

- **Conditional trays only:**
  - Apply VLE constraints ($Y_n=\text{True}$) or not ($Y_n=\text{False}$)
  - Use disjunctions as modeling tool.

---

[Diagram showing the flow of materials through the column with labels for Light Product, Feed, Heavy Product, Condenser Tray, Rectification Trays, Feed Tray, Stripping Trays, Reboiler Tray, and Vapor/Liquid Flow phases.]

- Equilibrium Stage
- Non-equilibrium Stage
- Vapor Flow
- Liquid Flow
Example GDP

GDP Formulation
Mixture: Methanol/Ethanol/water
Feed Flow = 10 mol/sec
Feed composition = 0.2/0.2/0.6
P = 1.01 bar
Product Specification:
products composition reversible model
Upper bound No. Trays: 60
Ideal/Wilson models

Used Logic-based OA

Methanol/ethanol/water - GDP: fixed tray location
Preprocessing Phase: NLP tray-by-tray Models

<table>
<thead>
<tr>
<th>Continuous Variables</th>
<th>1597</th>
</tr>
</thead>
<tbody>
<tr>
<td>Constraints</td>
<td>1544</td>
</tr>
<tr>
<td>Total CPU time (s)</td>
<td>1.12</td>
</tr>
</tbody>
</table>

Model Description

<table>
<thead>
<tr>
<th>Continuous Variables</th>
<th>2933</th>
</tr>
</thead>
<tbody>
<tr>
<td>Binary Variables</td>
<td>60</td>
</tr>
<tr>
<td>Constraints</td>
<td>2862</td>
</tr>
<tr>
<td>Nonlinear nonzero elements</td>
<td>5656</td>
</tr>
<tr>
<td>Number of iterations</td>
<td>10</td>
</tr>
<tr>
<td>NLP CPU time (s)</td>
<td>9.14</td>
</tr>
<tr>
<td>MILP CPU time (s)</td>
<td>16.97</td>
</tr>
<tr>
<td>Total CPU time (s)</td>
<td>401</td>
</tr>
</tbody>
</table>

Optimal Solution

| Total number of trays | 41   |
| Feed tray             | 20   |
| Column diameter (m)   | 0.51 |
| Condenser duty (KJ/s) | 387.4|
| Reboiler duty (KJ/s)  | 386.5|
| Objective value ($/yr)| 117,600|

\*GAMS PIII, 667 MHz. with 256 MB of RAM.

\*CONOPT2 NLP subproblems/ CPLEX MILP subproblems.
Reactive Distillation

Extension Single Column GDP Model

- Conditional Trays:
  - Active Trays
    - *Separation with reaction* may take place
      - Positive liquid holdup
    - *Separation only* may take place
      - Liquid holdup equals zero
  - Inactive Trays
    - Input-Output operation with *no mass transfer and no reaction*

Jackson & Grossmann (2001)
Example: Metathesis of Pentene

Conversion of 2-cis-pentene into 2-cis-butene and 3-cis-hexene:

\[ 2C_5H_{10} \leftrightarrow C_4H_8 + C_6H_{12} \]

**GDP Model:** 25 discrete variables
731 continuous variables
730 constraints

- **Annualized Cost:** $1.167 \times 10^6 per year
- **Design/Operating Parameters:**
  - 21 Trays; 5 Feeds
  - Column Diameter = 3.8ft
  - Column Height = 107ft
  - Boilup = 0.374
  - Reflux = 0.811
  - Reboiler Duty = 153 kW
  - Condenser Duty = 984 kW
- **Reaction Zone:**
  - Trays 1 – 18
  - Total Liquid Holdup = 752 ft$^3$
  - 90% Conversion of Pentene
Synthesis of complex distillation systems

Mariana Bartfeld, Pio Aguirre/INGAR

Superstructure Representation
- Suitable for zeotropic and azeotropic mixtures
- General and automatically generated
- Includes thermodynamic information
- Embeds many possible alternative designs

Superstructure Formulation
GDP formulation

Solution Procedure
- Decomposition algorithm (decision levels)
  - First level: selection of sections
  - Second level: selection of trays in existent sections
- Initialization phase: reversible sequence approximation
- Robust and effective solutions
State Task Network

Andrecovich, Westerberg (1985)

Sharp separation 4 components
State Equipment Network (SEN)


Sharp separation 4 components

STATE DEFINITION

S1- A, AB, ABC
S2- BCD, CD, D
S3- ABC
S4- BCD, CD
S5- AB
S6- CD
S7- BCD, CD, ABC
S8- A
S9- D
S10- CD, D, BC, C
S11- B, BC, A, AB, C
S12- CD, BC
S13- BC, AB
S14- C, D
S15- A, B C
S16- AB, BC, CD
S17- A, B, C
S18- B, C, D

TASKS
Superstructure for Complex Distillation Rigorous Model

Generated with the **State-Task-Network (STN)** (Sargent, 1998)

**STN Representation**
(4 Component Zeotropic Mixture)

**Sargent-Gaminibandara Superstructure**
(4 Component Zeotropic Mixture)
Superstructure Zeotropic Mixtures

Bartfeld, Aguirre, Grossmann (2004)

Based on the **Reversible Distillation Sequence Model (RDSM)** (Fonyo, 1974)

*Motivated by thermodynamic initialization scheme*

Automatically generated with the **State-Task-Representation (STN)**

Contains $2NC-1-1$ columns and $NC-1$ level

**RDSM-based STN Representation**

(4 Component Zeotropic Mixture)

Avoid mixing intermediates
Modification for Azeotropic Mixtures

RDSM-based STN cannot be defined a priori

**Composition diagram** needed

Azeotrope recycled
Mapping to Specific Designs
Discrete Decisions

Two hierarchical levels
1. Selection sections
2. Selection Trays

Selection of sections ➔ Configuration
- If section selected ➔ \( Y_s = True \)
- If section not selected ➔ \( Y_s = False \)
Configuration Model Formulation

\[ \begin{align*}
\text{min} & \quad z = TAC \\
\text{s.t.} & \quad g(x) \leq 0 \\
& \quad h(x) = 0
\end{align*} \]  

Objective Function

Overall Process Constraints

Tray Boolean Variables

Section Boolean Variables

DISJUNCTION

\[
\begin{align*}
f_{n,j}^L &= f(T_n, P_n, x_{n,j}) \\
f_{n,j}^V &= f(T_n, P_n, y_{n,j}) \\
f_{n,j} &= f_{n,j}^V \\
T_n^V &= T_n^L \\
\text{LIQ}_{n,j} &= L_n x_{n,j} \\
\text{VAP}_{n,j} &= V_n y_{n,j} \\
\text{stg}_n &= 1
\end{align*}
\]

\[
\begin{align*}
W_n \\
f_{n,j}^L = 0 \\
f_{n,j}^V = 0 \\
T_n^V = T_{n+1}^V \\
T_n^L = T_{n+1}^L \\
V_n = V_{n+1} \\
L_n = L_{n+1} \\
x_{n,j} = x_{n-1,j} \\
y_{n,j} = y_{n+1,j} \\
\text{stg}_n = 0
\end{align*}
\]

\[
\begin{align*}
\text{stg}_n = \sum_{n \in \sec_s} \text{stg}_n \\
\forall n \in \sec_s
\end{align*}
\]

Logic Relationships

\[
\begin{align*}
\Omega(Y_s) &= \text{True} \\
\Omega(W_s) &= \text{True}
\end{align*}
\]

\[
x \in X, Y_s, W_n \in \{\text{True, False}\}
\]
Detailed Cost Functions

**Annual Cost**

\[ TAC = C_{op} + \frac{C_{inv}}{T_{dep}} \]

**Operating Cost**

\[ C_{op} = \frac{Q_c}{C_p\text{agua}} \Delta T_{con} C_{agua} + \frac{Q_h}{\Delta H_{vap}} C_{vapor} \]

**Investment Cost**

\[ C_{inv} = C_{col} + C_{tray} + C_{reb} + C_{cond} \]

**Column Cost**

\[ C_{col} = k_{col} nt D_{col}^{1.066} h_{tray}^{0.802} \]

**Tray costs**

\[ C_{tray} = k_{tray} nt D_{col}^{1.55} h_{tray} \]

**Reboiler cost**

\[ C_{reb} = k_{reb} A_{reb}^{0.65} \]

**Condenser Cost**

\[ C_{cond} = k_{cond} A_{cond}^{0.65} \]

\[ D_{col} \geq D_{tray n} \]

\[ D_{tray n} = \sqrt{k_d V_n \left( \sum_i P M_i y_{n,i} \right)^{0.5} \left( \frac{T_{vapor} R}{p} \right)^{0.5}} \]
Solution Strategy

Preprocessing Phase

GDP Section Problem

GDP Tray Problem

- Initialization Phase -
  NLP Problems

- Selection of Sections -
  MILP Problem

- Selection of Trays -
  MILP Problem

Reduced NLP Problem

Algorithm Cycle

Aggregate NLP
NLP fixed max number trays

Fixed Max Number Trays

Fixed Number Sections
Zeotropic Example (1)

**Problem specs**
- Mixture: N-pentane/ N-hexane/ N-heptane
- Feed composition: 0.33/ 0.33/ 0.34
- Feed: 10 moles/s
- Pressure: 1 atm
- Max no trays: 15 (each section)
- Min purity: 98%
- Ideal thermodynamics

**GDP Model**
- Discrete Variables: 96
- Continuous Variables: 3301
- Constraints: 3230

**Initialization**

**Superstructure**
Zeotropic Example (2)

Optimal Configuration
$140,880 /yr

All sections selected

Optimal Design

<table>
<thead>
<tr>
<th>Annual cost ($/year)</th>
<th>140,880</th>
</tr>
</thead>
<tbody>
<tr>
<td>Preprocessing(min)</td>
<td>2.20</td>
</tr>
<tr>
<td>Subproblems NLP (min)</td>
<td>6.97</td>
</tr>
<tr>
<td>Subproblems MILP (min)</td>
<td>2.29</td>
</tr>
<tr>
<td>Iterations</td>
<td>5</td>
</tr>
<tr>
<td>Total solution time (min)</td>
<td>11.46</td>
</tr>
</tbody>
</table>

667MHz. Pentium III PC
**Zeotropic Example (3)**

**Optimal Configuration**

**$140,880 /yr**

**Configuration Side-Rectifier** $143,440 /yr

**Direct Sequence** $145,040 /yr

**Optimal Design**

<table>
<thead>
<tr>
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</tr>
<tr>
<td>Total solution time (min)</td>
<td>11.46</td>
</tr>
</tbody>
</table>

667MHz. Pentium III PC
Azeotropic Example

Problem Specs

Mixture: Methanol/ Ethanol/ Water
Feed composition: 0.5/ 0.3/ 0.2
Feed: 10 moles/s
Pressure: 1 atm
Max no. trays: 20 (per section)
Min purity: 95%
Ideal/Wilson models

Superstructure

Initialization

GDP Model

Discrete Variables 210
Continuous Variables 9025
Constraints 8996

Bartfeld, Aguirre, Grossmann (2004)
Product Specifications 95%
Optimal Configuration $318,400 /yr

Profiles Optimal Configuration

Optimal Solution

<table>
<thead>
<tr>
<th>Annual Cost ($/year)</th>
<th>318,400</th>
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</thead>
<tbody>
<tr>
<td>Preprocessing (min)</td>
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<td>Subproblems MILP (min)</td>
<td>3.70</td>
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<tr>
<td>Iterations</td>
<td>3</td>
</tr>
<tr>
<td>Total Solution Time (min)</td>
<td>46.01</td>
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</tbody>
</table>

667MHz. Pentium III PC

Azeotropic Example

Profiles Optimal Configuration

Optimal Solution

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</tr>
<tr>
<td>Total Solution Time (min)</td>
<td>46.01</td>
</tr>
</tbody>
</table>

667MHz. Pentium III PC
**STATES:** Intensive and extensive physical and chemical properties of a stream.

- Quantitative (composition, temperature)
- Qualitative (phase, components present)

**TASKS:** Physical or chemical transformations between adjacent states (momentum, heat and mass transfer operations).

- Permanent- Valid throughout flowsheet.
- Conditional- May not exist for a given flowsheet.

**EQUIPMENT:** Physical device that executes a task (design equations and parameters)

- Permanent or Conditional.
State Task Network

• First step: State and Task Identification in process flowsheet.

States:
1. A Raw, V, Low P
2. A mixed, V, Low P
3. A mixed, V, Low P to T3
4. A mixed, V, Low P to T4
5. A, V, High P form T3
6. A, V, High P form T4
7. A, V, High P, to preheat
9. A, V, to packed reactor
10. A+B, V to mixer T10
11. A, V, to PFR
12. A+B, V to mixer T10
13. A+B, V to cooler
16. A, V, low P
17. A+B, L, to distillation
18. B, L, to Final Product
19. A+B, V from PFR
20. A+B, high P
21. A+B, V, to waste product

Tasks:
1. Mix recirc A and raw A
2. Split feed mixture
3. Compress in single stage
4. Compress in two stages
5. Mix compressed streams and recycle.
6. Preheat for reaction
7. Split to reactors
8. React A→B in vapor phase in PFR
9. React A→B in vapor phase with catalizer C in packed reactor
10. Mix reactor outlets, Vapor
11. Condense stream
12. Flash A+B: A+B vapor, B liquid
13. Distillate A+B: A liquid, B liquid
14. Compress col. vapor outlet
15. Purge vapor stream
OTOE Assignment for STN

• Predetermined Equipment Assignment: One Task One Equipment
VTE Assignment for STN

- Assignment left over for optimization: Variable Task Equipment
State Equipment Network (SEN)

VTE:
- Preheat feed to reactor
  - or -
  Cool reactor outlet
  - or -
  Vaporize recycle from distillation
- React A→B (liquid phase)
  - or -
  React A-cat→B in packed reactor (vapor phase)
- Compress Recycle
  - or -
  Compress Feed

Carnegie Mellon
• **Boolean Variable $Y_t$:**
  * True- Task exists, task and equipment equations apply
  * False- Equipment does not exist. A subset of variables is set to zero.

\[
\min \sum_{t \in T} c_t + \sum_{s \in S} \alpha_s x_s \\
\text{s.t. } g_i(d_j, z_t, x_s, x_{s'}) \leq 0 \quad \forall j' \in Q_t, \quad t \in T_P \\
\quad c_i = f(d_j, z_t) \quad \forall s \in I_t, \quad s' \in O_t \\
\left[ \frac{Y_t}{g_i(d_j, z_t, x_s, x_{s'}) \leq 0} \right] \quad \forall j' \in Q_t \quad \left[ \frac{d_j = z_t = 0}{x_s = x_{s'} = 0} \right] \quad \forall s \in I_t, \quad s' \in O_t \\
\Omega(Y) = \text{True}
\]

\[
d \in D, z \in Z, x \in X \quad Y_t = \{\text{True, False}\}
\]
GDP Model for SEN

- Boolean $U_j$ for equipment existence.
- Boolean Variable $V_{jt}$:
  * True- Apply design equations for task $t$.
  * False- Do not apply design equations for task $t$.

$$\min \sum_{j \in E \in T} c_{jt} + \sum_{s \in S} \alpha_s x_s$$

s.t.

$$\left\{ \begin{array}{l}
V_{jt} \\
U_j \\
V_{jt}
\end{array} \right\} \begin{array}{l}
p_j(d_j, z_t, x_s, x_s') \leq 0 \\
p_j(d_j, z_t, x_s, x_s') \leq 0 \\
c_j = f(d_j, z_t)
\end{array} \begin{array}{l}
V_{jt} \\
U_j \\
V_{jt}
\end{array} \begin{array}{l}
V_{jt} \\
U_j \\
V_{jt}
\end{array} \begin{array}{l}
\neg U_j \\
z_t = d_j = 0 \\
x_s = x_s' = 0
\end{array} \begin{array}{l}
\Omega(V, U) = True \\
d \in D, z \in Z, x \in X, \quad V_{jt} = \{True, False\}, U_j = \{True, False\}
\end{array}$$
Theoretical Properties

- Model comparison (STN vs. SEN):
  - One Task - One Equipment assignments lead to simpler disjunctive models
  - SEN is equivalent to STN / OTOE if each equipment is allowed to perform only one task, provided the same tasks appear in both
  - STN / VTE leads to a different model than SEN. The same problem and same assignment (VTE) generate physically different superstructures
  - No model is inherently tighter than the other.
Flowsheet Synthesis: MINLP Approach (OTOE)

HDA process: 13 0-1 variables, 723 variables, 719 constraints  DICOPT: 7.5 secs

192 embedded flowsheets

LEGEND FOR INTERCONNECTION NODES
- Single choice stream splitter
- Multiple choice stream splitter
- Single choice stream mixer
- Multiple choice stream mixer

13 bin. var.  672 cont. var.  678 constr.
Profit = 4.057 M$/yr

Potential Problems:
1. Zero flows
2. Large dimensionality
Logic-based OA Algorithm

Basic idea: solve NLPs with only existing parts flowsheet

Turkay, Grossmann (1996)

Implemented in GAMS-LOGMIP
Example Superstructure Process Flowsheet (OTOE)

To apply Logic-based OA we require NLP subproblems to cover all units

Remark. Fewest number subproblems: set covering problem
Subproblem 1 (NLP): $859,000/yr

Feed 1 (cheap)

Subproblem 2 (NLP): $1,575,000/yr

Feed 2 (exp.)

All units covered => MILP Master 1: $1,868,000/yr
Subproblem 3 (NLP): $1,794,000/yr

MILP Master 2: $1,741,000/yr (with integer cut)

Since $1,741,000/yr < $1,794,000/yr  STOP!
Process Flowsheet Synthesis

Superstructure Vinyl Chloride Monomer  *(Turkay & Grossmann, 1997)*

---

**Major options:**
- **Direct Chlorination vs. Oxychlorination**
- **Air vs. Oxygen**
- **Pressure Pyrolysis**
- **Separation sequence**

**Optimization with discontinuous cost models:**
- Multiple size regions
- Pressure, temperature factors
Optimal Solution  (CPU-time: 3.8min)

Profit=$75.3 million/yr

<table>
<thead>
<tr>
<th>Item</th>
<th>Flowsheet 1</th>
<th>Flowsheet 2</th>
<th>Master Pr. 1</th>
<th>Flowsheet 3</th>
<th>Master Pr. 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Binary var.</td>
<td>162</td>
<td>168</td>
<td>259</td>
<td>168</td>
<td>259</td>
</tr>
<tr>
<td>Continuous var.</td>
<td>879</td>
<td>883</td>
<td>1715</td>
<td>883</td>
<td>1822</td>
</tr>
<tr>
<td>Constraints</td>
<td>699</td>
<td>703</td>
<td>1750</td>
<td>703</td>
<td>1858</td>
</tr>
<tr>
<td>Profit ($M/yr)</td>
<td>27.678</td>
<td>75.283</td>
<td>82.763</td>
<td>71.809</td>
<td>65.262</td>
</tr>
<tr>
<td>Major Iterations</td>
<td>3</td>
<td>3</td>
<td>N/A</td>
<td>3</td>
<td>N/A</td>
</tr>
<tr>
<td>CPU time (sec)</td>
<td>88.00</td>
<td>64.99</td>
<td>8.24</td>
<td>53.76</td>
<td>13.21</td>
</tr>
</tbody>
</table>
Biomass emerging as important renewable

US Energy Sources

- **Renewable Energy**: 7%
- **Solar Energy**: 1%
- **Hydroelectric**: 36%
- **Geothermal**: 5%
- **Wind Energy**: 5%
- **Biomass**: 53%

Other Sources:
- **Petroleum**: 40%
- **Natural Gas**: 23%
- **Coal**: 22%

**Note**: Sum of components may not equal 100% due to independent rounding.

## Process Design Challenges in Bioethanol

### Energy consumption corn-based process level:

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

### Water consumption corn based - process level:

<table>
<thead>
<tr>
<th>Author (year)</th>
<th>Water consumption (gal/gal ethanol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gallager (2005) First plants</td>
<td>11</td>
</tr>
<tr>
<td>Philips (1998)</td>
<td>5.8</td>
</tr>
<tr>
<td>MATP (2008) Old plants in 2006</td>
<td>4.6</td>
</tr>
<tr>
<td>MATP (2008) New plants</td>
<td>3.4</td>
</tr>
</tbody>
</table>
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)

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

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Required operations

Solids drying
Mechanical press before/after Beer column

Ethanol purification
Molecular Sieves vs Corn Grits
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
Optimized Structure

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**

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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)
Cellulosic Switchgrass and Microalgae highest yield (gal/acre)

Note: Switchgrass almost 3 times yield than Corn
Lignocellulosic Bioethanol

a) Thermochemical Process \((gasification)\)

\[
\text{Gasification} \rightarrow \text{Gas clean-up} \rightarrow \text{Fermentation or Catalytic} \rightarrow \text{Ethanol Recovery} \rightarrow \text{Power-Heat} \rightarrow \text{Electricity}
\]

b) Hydrolysis Process \((fermentation)\)

\[
\text{Biomass Pretreatment} \rightarrow \text{Cellulosic Hydrolysis} \rightarrow \text{Sugar Fermentation} \rightarrow \text{Ethanol Recovery} \rightarrow \text{Wastewater Power-Heat} \rightarrow \text{Electricity}
\]

Challenge:

Many alternative flowsheets
Superstructure Thermochemical Bioethanol

Ethanol via gasification

Gasification
- Direct Gasification
- Indirect Gasification

Reforming
- Steam Reforming
- Partial Oxidation

Clean up
- Wet solids removal
- Filter
- HBC removal
- WGSR
- Bypass
- PSA H2

CO/H2 Adj.
- MEA
- Sour gases removal
- PSA, CO2 Removal
- Membrane CO2

Fermentation
- Rectification
- Adsorption
- Fermentation
- Molecular Sieves
- Pervaporation

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

Catalytic
- Direct Sequence
- Indirect sequence

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

Solution Strategy Energy Optimization

Decomposition of GDP in 8 subproblems
Decision levels: Gasifier
- Removal HCs
- Reaction of Syn Gas

Heat integration and economic evaluation
Optimal Design of Lignocellulosic Ethanol Plant

Ethanol: $0.81/gal (no H₂ credits)
$0.42/gal (H₂ credits)

Low cost is due to H₂ production

$67.5 Million/yr
1,996 Btu/gal (< 1/10th of corn!)

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

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Optimal Flowsheet

$48 \text{ Million/yr vs. } $67.5 \text{ Million/yr (gasification)}
Impact of Lignin

Orange: Energy consumed after superstructure optimization with heat integration.
Red: Energy consumed after the contribution of lignin
Blue: Cooling water requirements after heat integration
Bioethanol Plant: no water management

Ahmetovic, Martin, Grossmann (2009)
Optimal Water Network: Corn Ethanol


1.5 vs 3.4

Freshwater

Fermentor

Solids removal

Organics removal

TDS removal

Discharge

Reduction freshwater from 9.07 to 1.17!

Evolution of Water Consumption

- a- Superstructure opt.
- b- Supers. + HEN
- c- Supers. + HEN + Mult.
- d- Supers. + HEN + Mult (opt. reflux ratio)

Synergy with Heat Recovery
Optimal Water Network: Lignocellulosic Ethanol

Gal. Water/Gal. Ethanol = 4.2

Cellulosic Bioethanol via Gasification

Optimal Water Network: Lignocellulosic Ethanol


Cellulosic Bioethanol via Hydrolisis
Table Summary of results [6-10]

<table>
<thead>
<tr>
<th></th>
<th>Ethanol (Hydrolysis)</th>
<th>Ethanol (Gasification &amp; Catalysis)</th>
<th>Ethanol (Gasification &amp; Fermentation)</th>
<th>FT-Diesel</th>
<th>Hydrogen (Cooking)</th>
<th>Biodiesel (Algae)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>A</strong> Total investment ($MM)</td>
<td>161</td>
<td>335</td>
<td>260</td>
<td>212</td>
<td>148</td>
<td>17</td>
</tr>
<tr>
<td><strong>B</strong> Capacity (MMgal/yr)</td>
<td>60</td>
<td>60</td>
<td>60</td>
<td>60</td>
<td>60'</td>
<td>72</td>
</tr>
<tr>
<td><strong>C</strong> Biofuel yield (kg/kg met)</td>
<td>0.28</td>
<td>0.20</td>
<td>0.33</td>
<td>0.24</td>
<td>0.11</td>
<td>0.96</td>
</tr>
<tr>
<td><strong>D</strong> Production cost ($/gal)</td>
<td>0.80</td>
<td>0.41</td>
<td>0.81</td>
<td>0.72</td>
<td>0.68'</td>
<td>0.70</td>
</tr>
<tr>
<td><strong>E</strong> Water consumption (gal/gal)</td>
<td>1.66</td>
<td>0.36</td>
<td>1.59</td>
<td>--</td>
<td>--</td>
<td>0.33</td>
</tr>
<tr>
<td><strong>F</strong> Energy consumption (MJ/gal)</td>
<td>-10.2</td>
<td>-9.5</td>
<td>27.2</td>
<td>-60.0</td>
<td>-3.84'</td>
<td>1.94</td>
</tr>
<tr>
<td></td>
<td>Energy CO2</td>
<td>Hydrogen Glycerol</td>
<td>Hydrogen Glycerol</td>
<td>Glycerol</td>
<td>Energy Glycerol</td>
<td>Fertilizer</td>
</tr>
</tbody>
</table>

(*) kg instead of gal

Sequential Modular Simulators

- Equipment libraries data bases
- Component property data bases
- Properties estimation

Numerical methods specifically developed for each process unit. Including Flash calculations in all the streams.

Initialization methods specifically design for each unit.

Rigid Input-output structure: Lack of flexibility. Convergence of recycles based on fixed point or quasi-Newton (Broyden) methods.

Very robust and reliable.

Equation Based Simulators

There is no difference between equations. The complete system is represented and solved by a set of equations without taking into account where they come from.

In general, no specific initialization methods.


Faster, and more flexible but less robust and reliable.

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Generalized Disjunctive Model

Integration with Process Simulators (implicit functions)

\[
\begin{align*}
\min : & \quad f(x_I, x_D, u) \\
\text{s.t.} & \quad r_I(x_I, x_D, u) = 0 \\
& \quad s_E(x_I, x_D, u) = 0 \\
& \quad s_E(x_I, x_D, u) \leq 0 \\
& \quad Y_{i,j} \\
\bigvee_{i \in D_j} & \quad h_{I,i,j}(x_I, x_D, u) = 0 \\
& \quad h_{E,i,j}(x_I, x_D, u) = 0 \\
& \quad g_{E,i,j}(x_I, x_D, u) \leq 0 \\
& \quad \Omega(Y) = \text{True} \\
& \quad x_I \in X \subseteq \mathbb{R}^n \\
& \quad Y \in \{\text{True, False}\}^m
\end{align*}
\]

Objective Function (i.e. total annual cost)

Implicit constraints common to all the alternatives

Explicit constraints common to all the alternatives

Implicit constraints depending on the boolean $Y_{ij}$

Explicit constraints depending on the boolean $Y_{ij}$

Logical relationships
\[ \min: f(x_I, x_D, u) \]

\text{s.t.} \begin{align*}
    r_I(x_I, x_D, u) &= 0 \\
    s_E(x_I, x_D, u) &= 0 \\
    s_E(x_I, x_D, u) &\leq 0 \\
    \forall j \in J \\
    \left[ \begin{array}{c}
    Y_{i,j} \\
    h_I(x_I, x_D, u) = 0 \\
    h_E(x_I, x_D, u) = 0 \\
    g_E(x_I, x_D, u) \leq 0
    \end{array} \right]
\end{align*}

\[ \Omega(Y) = \text{True} \]

\[ x_I \in X \subseteq \mathbb{R}^n \]

\[ Y \in \{\text{True, False}\}^m \]

**Disjunctive Representation**

\( x_I \) **Independent variables**: Specifications or degrees of freedom in the modular process simulator (or any other third party program). The user has a complete control over these variables.

\( x_D \) **Dependent variables**. They can only be read. Their value depend on the \( x_I \) variables.

\( u \) **variables that must be fixed**. The user has only an indirect control of these variables (i.e. trays in a column).
Algorithms

Regular and Disjunctive Branch and Bound (Gupta & Ravindran, 1985; Lee & Grossmann, 2000)

Solve series of NLP problems in a tree search (no Master needed)

Outer Approximation – MINLP reformulation - (Duran and Grossmann, )
Logic Based Outer Approximation (Turkay & Grossmann, 1996)
Modeling and Decomposition (Kocis & Grossmann, 1989)

LP-NLP Based Branch and Bound (Quesada and Grossmann, 1992)
Logic LP-NLP Based Branch and Bound

- Iterate between NLPs and Master (MILP) problems.
- In Outer Approximation the Master is solved to optimality in each major iteration.
- In LP-NLP based branch and bound the an NLP problem is solved when an Integer solution is found in the tree search of Master problems, all open nodes in the Master are then updated.
Solution Algorithms

Step 1. In the process simulator:

If the topology is fixed:

Select the independent variables (specifications). Chose a set of variables that makes that the simulation converges easily.
-Difficult constraints or difficult specifications should be done through external constraints-.

If the topology is variable: (not all the units necessarily exist in a feasible flowsheet)

It is necessary to study of each unit in order to prevent unexpected behavior, i.e. Lack of convergence due to zero flows.
If possible select the variables that minimizes (or avoid) those problems.

In some situations it would be necessary especial algorithms .
For process synthesis a good option are the “logic based algorithms”
(Turkay and Grossmann, 1996), (Kocis and Grossmann, 1989)
Step 2.

a. In the disjunctions there are no implicit equations:
   Reformulate to MINLP using Big M or Convex Hull.

b. In the disjunctions there are implicit equations, but they do not affect the topology
   Reformulate to MINLP using a Big M reformulation.

c. In the disjunctions there are implicit equations that modify the topology
   Solve each of the fixed topology NLP subproblems, or the ‘main’ subproblem
   and perform sub-lagrangian optimizations of the other units. (Logic Based Algorithms)

Solve the following NLP (r-MINLP).

\[
\begin{align*}
\min \quad & f(x_I, x_D, u) \\
\text{s.t.} \quad & r_I(x_I, x_D, u) = 0 \\
& r_E(x_I, x_D, u) = 0 \\
& s_E(x_I, x_D, u) \leq 0 \\
& h^*_{E,i,j}(x_I, x_D, u, y_{i,j}) = 0 \\
& g^*_{E,i,j}(x_I, x_D, u, y_{i,j}) \leq 0 \\
& Ay - b \leq 0 \\
& 0 \leq y \leq 1
\end{align*}
\]

Implicit equations (i.e. process simulator)
Big M, convex hull reformulation or fixed topology sub-problem
Algebraic representation of logical equations, in terms of binary variables
Step 3.

Generate (if necessary) the following Master MILP Problem

\[
\begin{align*}
\text{min} \quad & \alpha + \Pi^T (s_1 + s_2 + s_3 + s_4) \\
\text{subject to} \quad & \alpha \geq f[x_I^k, x_D(x_I^k), u] + \nabla_{x_I} f[x_I^k, x_D(x_I^k), u] (x_I - x_I^k) \\
& \lambda_1^T \nabla_{x_I} r_E[x_I^k, x_D(x_I^k), u] (x_I - x_I^k) \leq s_1 \\
& s_E[x_I^k, x_D(x_I^k), u] + \nabla_{x_I} s_E[x_I^k, x_D(x_I^k), u] (x_I - x_I^k) \leq s_2 \\
& \lambda_2^T \nabla_{x_I} h_E^*[x_I^k, x_D(x_I^k), u, y_{i,j}^k] \left( \frac{x_I^k - x_I}{y_{i,j}^k - y_{i,j}^k} \right) \leq s_3 \\
& g_E^*[x_I^k, x_D(x_I^k), u, y_{i,j}^k] + \nabla_{x_I} g_E^*[x_I^k, x_D(x_I^k), u, y_{i,j}^k] \left( \frac{x_I^k - x_I}{y_{i,j}^k - y_{i,j}^k} \right) \leq s_4 \\
& Ay - b \leq 0 \\
& y \in \{0, 1\}^m
\end{align*}
\]

Notes:
MILP only depends on \(x_I\) and slacks.

\(x_D = \Phi_I(x_I, u)\)

\(x_D\) is a function of \(x_I\). The linearization is done using the chain rule through the flowsheet or the implicit equations.

\[
\nabla_{x_I} f = \frac{\partial f}{\partial x_I} + \frac{\partial f}{\partial x_D} \frac{d x_D}{d x_I}
\]
Practical Implementation

All algorithms BB, OA, LP-NLP_BB were implemented in MATLAB 7.1.

All the steps: generation and solving Masters and NLPs problems are controlled from MATLAB.

Flowsheet simulated and converged in HYSYS.Plant 3.2

Auxiliary NLP and MILP solvers external to process simulator: MATLAB-TOMLAB (SNOPT 7, CONOPT 3, CPLEX 10)

Communication between MATLAB and HYSYS through ActiveX (Windows COM)

All other implicit equations (all but those in the process simulator) were developed as functions in MATLAB.
Set up communication MATLAB – HYSYS (Windows COM)

Choose Algorithm (BB, OA, LP-NLP_BB)
Set up initial NLP(s): (MINLP reformulations…)

Solve NLPs MATLAB-TOMLAB (conopt3, snopt7)

Generate Master MILP

Solve Master Problem MATLAB-TOMLAB (CPLEX)

Set up HYSYS Flowsheet.
Start from a converged flowsheet (external constraints can be violated)

HYSYS or other third party program or module

Derivatives

xI variables

xD variables
Example 1
Three heat exchangers network (Adapted from Turkay and Grossmann, 1996)

Some Data

<table>
<thead>
<tr>
<th>Stream</th>
<th>Tin (K)</th>
<th>Tout (K)</th>
<th>Cost ($/kW-year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hot</td>
<td>500</td>
<td>340</td>
<td></td>
</tr>
<tr>
<td>Cold</td>
<td>350</td>
<td>560</td>
<td></td>
</tr>
<tr>
<td>Cooling W</td>
<td>323</td>
<td>363</td>
<td>20</td>
</tr>
<tr>
<td>Heating V</td>
<td>557</td>
<td>557</td>
<td>80</td>
</tr>
</tbody>
</table>

Heat Exchanger U (kW/ m² K)
- E-101: 1.5
- E-102: 0.5
- E-103: 1.0

min: Cost utilities + Investment Cost

\[
\begin{align*}
Y_{j,1} & \geq I C_j = 2750 A_j^{0.6} + 3000 \\
Y_{j,2} & \geq I C_j = 1500 A_j^{0.6} + 15000 \\
Y_{j,3} & \geq I C_j = 600 A_j^{0.6} + 46500 \\
\end{align*}
\]

\[T_{\text{HotStreamT1}} \geq T_{\text{out \_ water}} + 10\]
**RESULTS**

Glycerol
100 kmol/h
76.85 ºC

DiPhenylC3
120 kmol/h
983.8 kW

Branch and Bound

Obj = 150322 $/year
Relaxed NLP (Big M) = 49259
Total NLP nodes = 37
CPU time (s) = 49.2
Solver = conopt (or snopt)

LP-NLP-BB

Obj = 150322 $/year
Relaxed NLP (Big M) = 49259
Total LP nodes = 17
Total NLP (subproblems) = 3
CPU time (s) = 4.01
Solver = snopt./Cplex

OA / ER / AP

Obj = 150322 $/year
Relaxed NLP (Big M) = 49259
Total Major iterations = 4
CPU time (s) = 5.18
Solver = snopt./Cplex
Example 2. DME Plant

Double Pipe
\[ A = f(T_{H}^{in}, T_{H}^{out}, T_{C}^{in}, T_{C}^{out}) \]
\[ \text{Cost}_{DP} = C_{DP}(A) \]

Multiple Pipe
\[ A = f(T_{H}^{in}, T_{H}^{out}, T_{C}^{in}, T_{C}^{out}) \]
\[ \text{Cost}_{MP} = C_{MP}(A) \]

Fixed Head
\[ A = f(T_{H}^{in}, T_{H}^{out}, T_{C}^{in}, T_{C}^{out}) \]
\[ \text{Cost}_{FH} = C_{FH}(A) \]

- \( 10 \leq A \leq 1000 \)

Air Cooler
\[ A = A(T_{in}^{s}, T_{out}^{s}, T_{in}^{Air}, T_{out}^{Air}, U_{Air}) \]
\[ \text{Cost} = C_{Air}(A) \]
\[ \text{Cost}_{UtilityAir} = 0 \]

HE_Water
\[ A = A(T_{in}^{s}, T_{out}^{s}, T_{in}^{W}, T_{out}^{W}, U_{W}) \]
\[ \text{Cost} = C_{TS}(A) \]
\[ \text{Cost}_{UtilityAir} = \text{Cost}_{Water} \]

261.5 kmol/h
1.01 bar
25 °C
\( x_{\text{MeOH}} = 0.8 \)
\( x_{\text{Water}} = 0.2 \)

137.3 kmol/h
\( x_{\text{MeOH}} = 0.995 \)
Example 2. DME Plant (cont.)

Recycled converged by the Optimizer

**Tray Column**
- \( \text{Size}_{\text{Vessel}} = f(N, L, V, \rho...) \)
- \( \text{Cost}_{\text{Vessel}} = f(H, D) \)
- \( \text{Cost}_{\text{Internals}} = F(N, \text{material}) \)
- \( D \geq 1 \text{ m} \)

**Packed Column**
- \( \text{Size}_{\text{Vessel}} = f(N, L, V, \rho...) \)
- \( \text{Cost}_{\text{Vessel}} = f(H, D) \)
- \( \text{Cost}_{\text{Internals}} = F(N, \text{material}) \)
- \( D \leq 1 \text{ m} \)
Optimal Solution

TAC = 1.002x10^6 $/year
Optimal Solution: \( 1.002 \times 10^6 \) $/year  
Initial Relaxed Solution: \( 9.45 \times 10^6 \) $/year (Gap 5.5\%)  
Reformulated to MINLP mixed Big M- convex hull

12 linear constraints
63 explicit non-linear constraints
72 variables (22 binary, 12 in the flowsheet)

39 implicit blocks of equations: sizing, cost estimation…
And the equation in the flowsheet (Hysys).

### LP-NLP_BB
- Total CPU time = 2423 s
- Number of NLPs = 9
- LP nodes = 111.
- Solvers: snopt, cplex

### Outer Approximation
- Total CPU time = 2219 s
- Number of Major iterations = 4
- Solvers: snopt, cplex

Remark: Most of the CPU time is spent estimating derivatives. However, typically the NLP takes 10-20 major iterations.
Rigorous Flowsheet Optimization using Process Simulators and Surrogate Models

Motivation

Perform flowsheet synthesis using models from process simulators

Black box models

- No access to the original code
- In some cases significant CPU computation time is required
- Usually derivatives are not available

In modular process simulators:
- No derivative information available
- Usually perturbation does not provide accurate values due to the noise introduced by the model

Caballero, Grossmann (2008)
Kriging Interpolation:

\[ y(x) = f(x) + Z(x) \]

Kriging assumes that errors are not independent but a function of x

\[ E(Z(x)) = 0 \]

\[ \text{cov}(Z(x_i), Z(x_j)) = \sigma^2 R(x_i, x_j) \]

\[ \sigma^2 = \text{Process Variance} \]

\[ R(x_i, x_j) = \exp\left(-\sum_{l=1}^{d} \theta_l |x_{i,l} - x_{j,l}|^p \right) \]

Spatial correlation function: No Euclidean

\[ \theta_l \geq 0; \ 0 \leq P_l \leq 2 \]

Include adjustable parameters

Due to these parameters it is not sensitive to the units of measurements

The final predictor for the new point \((x^{\text{new}}, y^{\text{new}})\)

\[ \hat{y}(x^{\text{new}}) = \bar{\mu} + r^T R^{-1} (y - 1\bar{\mu}) \]

\[ s^2(x^{\text{new}}) = \sigma^2 \left( 1 - r^T R^{-1} r + \frac{(1 - r^T R^{-1} r)^2}{1^T R^{-1} 1} \right) \]

Standard error predicted by the interpolator

(a non interpolation version is easy to implement as well)
Kriging Example

Actual function

Kriging interpolation based on the 33 points in figure

\[ z = 3(1 - x)^2 e^{-x^2} - (y + 1)^2 - 10\left(\frac{x}{5} - x^3 - y^5\right)e^{-(x^2 - y^2)} - \frac{1}{3}e^{-(x+1)^2 - y^2} \]
Kriging Example

Actual function

Krigeing interpolation

Errors predicted by the kriging
\[ z = 3(1-x)^2 e^{-x^2} - (y+1)^2 - 10\left(\frac{x}{5} - x^3 - y^5\right)e^{-(x^2-y^2)} - \frac{1}{3}e^{-(x+1)^2-y^2} \]

\[ \frac{\partial z(x, y)}{\partial x} \quad \text{Analytical} \]

\[ \frac{\partial z(x, y)}{\partial x} \quad \text{Calculated by kriging} \]
Algorithm

1. Select unit operation(s) to be substituted by a metamodel
2. Bounds on variables (as tight as possible)
3. Sampling

The sampling must be done to preserve the uniformity of the distribution and avoid ‘correlation’.

Latin Hypercube sampling, Hammersley, Halton or Sobol

\[ \max \min \sum_i \sum_j d_{i,j} \quad d_{i,j} = \text{distance between sample points i and j} \]

4. Generate kriging model

   Adjust parameters using an available NLP solver (SNOPT, CONOPT)

5. Validate kriging model: Cross validation

6. Optimization using the kriging metamodel instead of the selected unit operations

   (Using any NLP solver available i.e. SNOPT, CONOPT, KNITRO)

7. Refinement stage (optional):

8. Re-sampling and recalibration

9. Repeat from point 6 until convergence
Example: phthalic anhydride from o-xylene

Min : Total annual cost =
Fixed + variable costs
(compressor, pump, heater,
cooler, reactor, flash, column)

s.t. cost and sizing equations
ph. Anhydride > 0.99 (molar fraction)

(R1) \[ 3O_2 + C_8H_{10} \rightarrow 3H_2O + C_6H_4(CO_2)_2O \]
\text{o-xylene} \hspace{1cm} \text{phthalic anhydride}

(R2) \[ 7.5O_2 + C_8H_{10} \rightarrow C_4H_2O_3 + 4CO_2 + 4H_2O \]
\text{o-xylene} \hspace{1cm} \text{maleic anhydride}

(R3) \[ 10O_2 + C_8H_{10} \rightarrow 8CO_2 + 5H_2O \]
\text{o-xylene}

Plug flow reactor
substituted by kriging
metamodels

Number of sample points = 71
Convergence in two major iterations
Total CPU time = 169.9 s.; SOLVER = SNOPT7
Example: Optimal solution

Compressor 1303 kW

Air (1000 kmol/h)

183 °C, 334 kPa

O-xylene (3272 kmol/h)

Vapor fraction = 1

Reactor 144 x 0.5 m

123.4 °C

Heater 1795 kW

306.6 °C

396.8 °C

13790 kW

Cooler 4241 kW

71 °C

O-xylene 0.082 kmol/h

Oxygen 73.03 kmol/h

Nitrogen 790 kmol/h

Maleic Ah. 0.284 kmol/h

Phthalic Ah. 0.072 kmol/h

CO2 43.20 kmol/h

H2O 70.518 kmol/h

Maleic An. 5.49 kmol/h

Water 32.78 kmol/h

O-xylene 0.034 kmol/h

Rest < 0.001 kmol/h

22.36 kmol/h phthalic An.

Purity > 0.999

Distillation column 10 theoretical trays

Diameter = 1.06 m

1034 kW

1282 kW

Carnegie Mellon
Introduction & Motivation

Henao, Maravelias (2010)

The whole picture:
**Motivation**

Synthesis of methanol in a fixed bed multi-tube reactor:

- **Reactions**
  - \( CO_2 + 3 \cdot H_2 \rightarrow MeOH + H_2O \) (MSR)
  - \( CO + H_2O \rightarrow CO_2 + H_2 \) (WGS)

- **Reactor model:**
  - Adiabatic operation,
  - Total radial mix,
  - No axial diffusion,
  - Pressure drop as per Ergun,
  - Real mixture thermodynamics.

### Mass Balances
\[
\frac{dF_i}{dL} = \sum_{j=1}^{NR} a_{ij} \cdot \frac{p_j}{dL} = \frac{dF_i}{As_R \cdot d(L)}, \quad i = 1, \ldots, NC
\]

### Energy Balances
\[
q \cdot \Omega_R \cdot dL = d(F \cdot h) - d(F_{FT} \cdot h_{FT})
\]

### Kinetics
\[
r_j = f(C_1, \ldots, C_{NC}, T), \quad j = 1, \ldots, NR
\]
\[
C_i = F_i / (F \cdot \omega)
\]

### Heat transfer
\[
q = U \cdot (T_{FT} - T)
\]

### Geometry
\[
V_R = N_i \cdot \frac{\pi D_i^2}{4} \cdot L_R
\]
\[
\Omega_R = N_i \cdot \pi \cdot D_i
\]
\[
As_R = N_i \cdot \frac{\pi D_i^2}{4}
\]

### Hydraulics
\[
\frac{dP}{dL} = -\frac{1}{1000} \cdot \frac{\rho \cdot \nu_i \cdot (1 - \varepsilon) \cdot \left(\frac{150 \cdot (1 - \varepsilon)}{Re_p} + 1.75\right)}{\rho \cdot D_p \cdot \varepsilon^3}
\]
where
\[
Re_p = \frac{\varphi_p \cdot D_p \cdot \nu_i \cdot \rho}{\mu}
\]
\[
\nu_i = \frac{F_i}{As_R}
\]
\[
\frac{dP_{FT}}{dL} = \frac{\Delta P_{FT}}{L_R}
\]

### Thermo and transport properties
\[
h = f(T, P, x_1, \ldots, x_{NC})
\]
\[
h_{FT} = f(T_{FT}, P_{FT}, x_{i|FT}, \ldots, x_{NC|FT})
\]
\[
v = f(T, P, x_1, \ldots, x_{NC})
\]
\[
\mu = f(T, P, x_1, \ldots, x_{NC})
\]

- \( r_j \) – reaction rate
- \( h \) – molar enthalpy
- \( v \) – molar volume
- \( \mu \) – viscosity

---

175
Motivation

- What we really need is a mapping: $f$: inputs $\rightarrow$ outputs

Our approach: Replace complex unit models with surrogate models, relating only necessary variables while enforcing the same constraints.
**Surrogate Model Design**

*First-principles* unit model:
- \( I_{UM} \): Independent variable set (degrees of freedom),
- \( D_{UM} \): Dependent variable set,
- \( C_{UM} \): Connecting variable set (variables appearing in any other part of the problem),
- \( F_{UM} \): Fixed variable set (design specifications),

\[ I_{UM} \cap C_{UM} \cap F_{UM} \]

Implicit unit model mapping (simulation)

**Surrogate** unit model:
Enforce constraints between independent and connecting dependent variables
- \( I_{S} \): Independent variable set,
- \( D_{S} \): Dependent variable set,

\[ I_{S} = I_{UM} \setminus F_{UM} \]

\[ D_{S} = C_{UM} \cap D_{UM} = C_{UM} \setminus I_{UM} \]

Dimensionally reduced surrogate model mapping
Surrogate Model Design

- Fixed ($F_{UM}$) and connecting ($C_{UM}$) variables are given from problem are given
- There are multiple choices for independent ($I_{UM}$) variables
- Structurally non-singular model: perfect matching between dependent variables and equations†

Matching problem:
- $J$: Set of variables,
- $K$: Set of equations,
- $A$: Variable-equation incidence matrix,
- $x_{jk}$: Variable-equation matching variables
- $y_j$: Selection binaries defining $I_{UM}$
- $w_j$: Selection preference coefficients

Since $F_{UM} \subseteq I_{UM}$ $\Rightarrow$ $y_j = 1$, $\forall j \in F_{UM}$
Selection preferences to reduce number of surrogate variables; include connecting ($C_{UM}$) in $I_{UM}$

\[ I_S = I_{UM} \setminus F_{UM} \]
\[ D_S = C_{UM} \setminus I_{UM} \]

\[ |I_S| = |I_{UM}| - |F_{UM}| \]
\[ |D_S| = |C_{UM}| - |C_{UM} \cap I_{UM}| \]

\[ w_j >> 1 \ \forall j \in C_{UM} \]

† Bunus P. Fritzson P. Sim Tran Soc Mod & Sim Int 2004; 80: 321
**Surrogate Model Design**

- Fixed ($F_{UM}$) and connecting ($C_{UM}$) variables are given from problem are given.
- There are multiple choices for independent ($I_{UM}$) variables.
- Structurally non-singular model: perfect matching between dependent variables and equations\(^\dagger\)

**Matching problem:**
- \(J\): Set of variables,
- \(K\): Set of equations,
- \(A\): Variable-equation incidence matrix,
- \(x_{jk}\): Variable-equation matching variables
- \(y_j\): Selection binaries defining $I_{UM}$
- \(w_j\): Selection preference coefficients

Since $F_{UM} \subset I_{UM} \Rightarrow y_j = 1$, \(\forall j \in F_{UM}\)

Selection preferences to reduce number of surrogate variables; include connecting ($C_{UM}$) in $I_{UM}$

\[
\begin{align*}
|I_S| &= |I_{UM}| - |F_{UM}| \\
|D_S| &= |C_{UM}| - |C_{UM} \cap I_{UM}|
\end{align*}
\]

\[\max \sum_{j \in J} w_j \cdot y_j \quad \text{s.t.} \quad \begin{align*}
\sum_{j \in (j,k) \in A} x_{jk} &= 1 & \forall k \in K \\
\sum_{k \in (j,k) \in A} x_{jk} &= 1 - y_j & \forall j \in J \\
x_{jk}, y_j & \in \{0,1\}
\end{align*}\]

\(w_j >> 1 \quad \forall j \in C_{UM}\)

\(\dagger\) Bunus P. Fritzson P. *Sim Tran Soc Mod & Sim Int* 2004; 80: 321
Surrogate Model Design: Example

- Optimal design and operation of a homogeneous CSTR with fixed feed and $\Delta P$

CSTR optimization problem

\[
\begin{align*}
\text{max} & \quad f_{\text{obj}}(F_{c^* \rho}, V_R, Q_R) \\
\text{s.t.} & \quad f_{\text{CSTR}}(\ldots) = 0 \\
& \quad T_0 \leq T_{\text{max}}
\end{align*}
\]

CSTR detailed model

Mass balances

\[
F_{c^I} + V_R \cdot \sum_{r \in R} (V_R \cdot r_r) = F_{c^O}, \quad \forall C \in C
\]

Energy balance

\[
h_I \cdot \left( \sum_{c \in R} F_{c^I} \right) + Q_R = h_O \cdot \left( \sum_{c \in R} F_{c^O} \right)
\]

Additional expressions

\[
P_I - \Delta P_R = P_O \\
r_r = f^I \left( T_O \cdot \left[ C_{x^O} \right]_{r \in C} \right), \quad \forall r \in R \\
x_{c^I} \cdot \left( \sum_{c \in R} F_{c^I} \right) = F_{c^I}, \quad x_{c^O} \cdot \left( \sum_{c \in R} F_{c^O} \right) = F_{c^O}, \quad \forall C \in C
\]

\[
C_{c^O} = x_{c^O} / \rho_O
\]

\[
\begin{align*}
F_{UM} = & \{ T_I, P_I, [F_{c^I}]_{r \in C}, \Delta P_R \} \\
C_{UM} = & \{ T_O, F_{c^O}, V_R, Q_R \} \\
I_{UM} = & \{ T_I, P_I, [F_{c^I}]_{r \in C}, \Delta P_R, V_R, T_O \}
\end{align*}
\]

\[
\begin{align*}
D_S = & \{ F_{c^O}, Q_R \} \\
I_S = & \{ V_R, T_O \}
\end{align*}
\]
Surrogate Model Formulations

We assume $F_{UM} = \emptyset$,

General considerations for $I_{UM}, C_{UM}$

Incorporate linear equations of the original unit models:

**Stream Mixers**

**Stream Splitters**

**Compressors – Pumps – Turbines**

Mass balances

$$\sum_{c \in C} F_{c,s} = \sum_{s' \in S_u^O} F_{c,s'}, \quad \forall u \in U^M, \forall c \in C$$

Mass balances

$$F_{c,s} \cdot \xi_{s', u} = F_{c,s'}, \quad \forall u \in U^S, \forall s \in S_u^I, \forall s' \in S_u^O, \forall c \in C$$

Mass balances

$$\sum_{s \in S_u^I} F_{c,s} = \sum_{s' \in S_u^O} F_{c,s'}, \quad \forall u \in U^{CPT}, \forall c \in C$$

Additional expressions

$$\min_{s \in S_u^I} (P_s) = P_s, \quad \forall u \in U^M, \forall s' \in S_u^O$$

Additional expressions

$$\sum_{s \in S_u^I} \xi_{s', u} = 1, \quad \forall u \in U^S$$

Additional expressions

$$P_s + AP_{u} = P_{s'}, \quad \forall u \in U^{CPT}, \forall s \in S_u^I, \forall s' \in S_u^O$$

Multivariable mapping

$$T_s = f_{s,u}^T \left( \{F_{c,s}, T_s, P_s\}_{c \in C} \right), \quad \forall u \in U^M, \forall s' \in S_u^O$$

Multivariable mapping

$$T_s = f_{s,u}^T \left( \{F_{c,s}, T_s, P_s\}_{c \in C}, AP_{u}, \check{\epsilon}_u \right), \quad \forall u \in U^{CPT}, \forall s' \in S_u^O$$

Multivariable mapping

$$W_u = f_u^P \left( \{F_{c,s}, T_s, P_s\}_{c \in C}, AP_{u}, \check{\epsilon}_u \right), \quad \forall u \in U^{CPT}$$
Surrogate Model Formulations

- We assume $F_{UM} = \emptyset$.
- General considerations for $I_{UM}, C_{UM}$
- Incorporate linear equations of the original unit models:

**Expansion Valves**

Mass balances
$$\sum_{s \in S_u^I} F_{c,s} = \sum_{s' \in S_u^O} F_{c,s'}, \quad \forall u \in U^{EV}, \forall c \in C$$

Additional expressions
$$P_s - \Delta P_u = P_s', \quad \forall s \in S_u^I, \forall s' \in S_u^O$$

Multivariable mapping
$$T_s = f_{s,u}^{E} \left( \left[ F_{c,s}, T_s, P_s \right]_{s \in S_u^I}, \Delta P_u \right), \quad \forall u \in U^{EV}, \forall s' \in S_u^O$$

**Heaters-Coolers**

Mass balances
$$\sum_{s \in S_u^I} F_{c,s} = \sum_{s' \in S_u^O} F_{c,s'}, \quad \forall u \in U^{HC}, \forall c \in C$$

Additional expressions
$$P_s - \Delta P_u = P_s, \quad \forall s \in S_u^I, \forall s' \in S_u^O$$

Multivariable mapping
$$Q_u = f_{u}^{HC} \left( \left[ F_{c,s}, T_u, P_u \right]_{s \in S_u^I}, \Delta P_u, Q_u \right), \quad \forall u \in U^{HC}$$

**Flash Vessels**

Mass balances
$$\sum_{s \in S_u^I} F_{c,s} = \sum_{s' \in S_u^O} F_{c,s'}, \quad \forall u \in U^{FV}, \forall c \in C$$

Additional expressions
$$P_s - \Delta P_u = P_s, \quad \forall s \in S_u^I, \forall s' \in S_u^O$$

Multivariable mapping
$$F_{c,s} = f_{c,s,u}^{F} \left( \left[ F_{c,s}, T_s, P_s \right]_{s \in S_u^I}, \Delta P_u, Q_u \right), \quad \forall s' \in S_u^O, \forall c \in C$$

$$T_s = f_{s,u}^{F} \left( \left[ F_{c,s}, T_s, P_s \right]_{s \in S_u^I}, \Delta P_u, Q_u \right), \quad \forall u \in U^{FV}$$
### Surrogate Model Formulations

- We assume $F_{UM} = \emptyset$,
- General considerations for $I_{UM}, C_{UM}$
- Incorporate linear equations of the original unit models:

#### Distillation Columns (Isobaric)

<table>
<thead>
<tr>
<th>Mass balances</th>
<th>$\sum_{x=1}^{x} F_{c,s} = \sum_{x=1}^{x} F_{c,s'}$, $\forall u \in \mathbb{U}_{DC}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Additional expressions</td>
<td>$P_s - \Delta P_u = P_c$, $\forall u \in \mathbb{U}_{DC}$, $\forall s \in S^1$</td>
</tr>
<tr>
<td>$T_{cond} = T_c$, $\forall s' \in S^0 \setminus {o_2}$</td>
<td></td>
</tr>
<tr>
<td>Complementary multivariable mapping</td>
<td>$F_{c,s} = f_{c,s}^{F} \left[ F_{c,s}, T_{c}, P_{c}, I_{1}\right]<em>{s,s'}, \sqrt{u} \in \mathbb{U}</em>{DC}$, $\forall s' \in S^0 \setminus {o_2}$</td>
</tr>
<tr>
<td>$Q_{c,u} = f_{c,u}^{Q} \left[ F_{c,s}, T_{c}, P_{c}, I_{1}\right]<em>{s,s'}, \sqrt{u} \in \mathbb{U}</em>{DC}$</td>
<td></td>
</tr>
<tr>
<td>$Q_{s,u} = f_{s,u}^{Q} \left[ F_{c,s}, T_{c}, P_{c}, I_{1}\right]<em>{s,s'}, \sqrt{u} \in \mathbb{U}</em>{DC}$</td>
<td></td>
</tr>
<tr>
<td>$T_{s} = f_{s,u}^{T} \left[ F_{c,s}, T_{c}, P_{c}, I_{1}\right]<em>{s,s'}, \sqrt{u} \in \mathbb{U}</em>{DC}$, $\forall s' \in S^0 \setminus {o_2}$</td>
<td></td>
</tr>
</tbody>
</table>

#### Absorption Columns (Isobaric)

| Mass balances | $\sum_{x=1}^{x} F_{c,s} = \sum_{x=1}^{x} F_{c,s'}$, $\forall u \in \mathbb{U}_{MC}$ |
| Additional expressions | $\forall u \in \mathbb{U}_{MC}$, $\forall c \in C$ |
| $\min(P_i) - \Delta P_u = P_c$, $\forall u \in \mathbb{U}_{MC}$, $\forall s' \in S^0$ |
| Complementary multivariable mapping | $F_{c,s} = f_{c,s}^{F} \left[ F_{c,s}, T_{c}, P_{c}, I_{1}\right]_{s,s'}, \sqrt{u} \in \mathbb{U}_{MC}$, $\forall s' \in S^0 \setminus \{o_2\}$ |
| $T_{s} = f_{s,u}^{T} \left[ F_{c,s}, T_{c}, P_{c}, I_{1}\right]_{s,s'}, \sqrt{u} \in \mathbb{U}_{MC}$, $\forall s' \in S^0 \setminus \{o_2\}$ |

#### Reactors (Isothermali)

| Mass balances | $\sum_{x=1}^{x} F_{c,s} = \sum_{x=1}^{x} F_{c,s'}$, $\forall u \in \mathbb{U}_{R}$ |
| Additional expressions | $\forall c \in C$ |
| $P_s - \Delta P_u = P_c$, $\forall u \in \mathbb{U}_{R}$, $\forall s \in S^1$ |
| $T_{s} = T_c$, $\forall s \in S^1$ |
| Complementary multivariable mapping | $Q_{c,s} = f_{c,s}^{Q} \left[ F_{c,s}, T_{c}, P_{c}, I_{1}\right]_{s,s'}, \sqrt{u} \in \mathbb{U}_{R}$, $\forall s' \in S^0$ |
| $X_{s} = f_{s,u}^{X} \left[ F_{c,s}, T_{c}, P_{c}, I_{1}\right]_{s,s'}, \sqrt{u} \in \mathbb{U}_{R}$, $\forall r \in R$ |
Data Generation and Training

- The framework can be used with any fitting method
  - Linear models: fit split fraction, extend of reaction, etc.
  - Shortcut methods: fit key parameters
- We use artificial neural network (ANN) surrogates:
  - Simple structure and excellent fitting capabilities.
  - Reformulation properties
  - Network with a total of $K$ layers

Formulation:
- $u^0$: network input
- $u^K$: network output

$$u^k = f^k(W^k \cdot u^{k-1} + b^k), \quad k = 1, \ldots, K$$

where $u^k$ = layer $k$ output
- $W^k$ = layer $k$ weight matrix
- $b^k$ = layer $k$ bias vector
- $f^k(\cdot)$ = layer $k$ activation function
Data Generation and Training

- Data generation and surrogate fitting using MATLAB – ASPEN Plus:

**Flowchart**

- **I₅ data generation**
  - I₅ space sampling subroutine (Latin Hypercube)
  - Input matrix
  - Output matrix

- **D₄ data generation**
  - IS data generation
  - Unit.inp template
  - MATLAB - ASPEN interface sub-routine
  - Input matrix
  - M&E balance results
  - Unit.inp modified
  - Unit.out

- **Network training**
  - Data pre-processing subroutine (Scaling and Principal Component Analysis)
  - Neural Network Training sub-routine (Bayesian Regularization + Early stopping)
  - Neural Net adjustable parameter values

- **ASPEN PLUS calculation engine**
  - Unit.inp modified
  - Unit.out
Optimum design and operation of a homogeneous CSTR,

- Production of Maleic Anhydride,
  
  \[ C_6H_6 + 4.5O_2 \rightarrow C_4H_2O_5 + 2CO_2 + 2H_2O \]
  \[ C_4H_2O_3 + 3O_2 \rightarrow 4CO_2 + H_2O \]
  \[ C_6H_6 + 7.5O_2 \rightarrow 6CO_2 + 3H_2O \]

- Fixed feed \( F_{c_1}, T_I, P_I \) and pressure drop \( \Delta P \),

Objective: Find \( V_R \) and \( T_0 \) maximizing profit

Variable analysis:

\[
\begin{align*}
F_{UM} &= \{ T_I, P_I, [F_{c_1}]_{\forall c < C}, \Delta P_R \} \\
C_{UM} &= \{ T_O, F_{c_1, O}, V_R, Q_R \} \\
I_{UM} &= \{ T_I, P_I, [F_{c_1}]_{\forall c < C}, \Delta P_R, V_R, T_O \}
\end{align*}
\]

Original model: \(|I_{UM}| + |D_{UM}| = 45, \ |F_{UM}| = 9\)

Surrogate model: \(|I_S| + |D_S| = 4\)

Surrogate: ANN with 2 hidden layers, 5 neurons each

Optimum values:

- \( T_{O}[K] = 670 \)
- \( V_R[m^3] = 40 \)
Data Generation and Training: Example 2

- Solvent regeneration in amine based carbon capture
  - Detailed unit model (MESH) with ideal thermo package
  - Surrogate model: ANN fitting MESH-Amines thermo package
  - Fixed $N_s$, $N_r$, $T_{cond}$.
  - Variable analysis: $D_{S'} = \{F_{C,O_2}, c \in C; Q_{C_{Ru}}; Q_{R_{Ru}}; T_{O1}\}$
    $I_S = \{F_{C,s}, T_s, P_s, c \in C, s \in S^I_u; B_{Ru}\}$

- Original unit model (MESH & ideal thermo pkg)

- ANN surrogate model (fitted with Amine pkg)
**High-level Formulation Approach**

- Generate superstructure (engineering judgment, artificial intelligence, evolutionary design)
- Choose method to activate/de-activate unit models
  - Math programming with equilibrium constraints (Biegler et al.)
  - Disjunctive programming (Grossmann et al.)

\[
\begin{align*}
  h_u \left( \left[ F_{c,s}, T_s, P_s \right]_{s \in S_{u}}, \psi_u \right) &= Y_u \\
  g_u \left( \left[ F_{c,s}, T_s, P_s \right]_{s \in S_{u}}, \psi_u \right) &
  \leq 0 \\
  CC_u &= \gamma_u^{CC} \left( \left[ T_s, P_s \right]_{s \in S_{u}}, \psi_u \right) \\
  OPC_u &= \gamma_u^{OPC} \left( \psi_u \right)
\end{align*}
\]

\[
\begin{bmatrix}
  F_{c,s} = 0 & \forall c \in C \\
  T_s = 0 & \forall s \in S_u \\
  P_s = 0 \\
  \psi_u = 0 \\
  CC_u = 0, & OPC_u = 0
\end{bmatrix} \quad \forall u \in U^C
\]
What next for Process Synthesis and Design?

Three major issues:

1. **Uncertainty:**
   - Theory is available
     - (stochastic programming, robust optimization, flexibility analysis)
   - Major issue: computational

2. **Process intensification**
   - Limited cases process flowsheets, microsysytems
   - Major issue: representations

3. **Nonlinear process models**
   - To support process synthesis with complex models
   - Major issue: convergence

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Process Intensification: Original Methyl Acetate Flowsheet

Siirola (1988)
Process Intensification
Single Column Methyl Acetate Process

Acetic Acid

Catalyst

Methanol

Distillation Task G
Extractive Distillation Task F
Reactive Distillation Task E
Reaction Task A
Reactive Distillation Task B
Distillation Tasks C and D

Methyl Acetate

Water
Synthesis Multiproduct Batch Plant

(Lee, Grossmann, 2000)

A→ Mixing → Reaction → Crystallization → Drying → B

ABC

Tasks

Equipment

Unit 1
Cast Iron w/ Agitator

Unit 2
Stainless Steel w/ Agitator

Unit 3
Cast Iron Jacketed

Unit 4
Stainless Steel Jacketed w/ Agitator

Unit 5
Tray Dryer

More than 100 alternatives: each requires nonlinear optimization
Synthesis Multiproduct Batch Plant

Nonconvex GDP Model

\[
\min \text{COST} = \sum_{j=1}^{M} N_{ij} C_{j} + \sum_{j} CS_{j}
\]

subject to

\[
V_{t}^{T} \geq B_{i} S_{it}, \quad i = 1, \ldots, N_{p}; t = 1, \ldots, T
\]

\[
pt_{ij} = \sum_{t \in t_{ij}} pty_{itj}, \quad i = 1, \ldots, N_{p}; j = 1, \ldots, M
\]

\[
n_{i} B_{i} \geq Q_{i}, \quad i = 1, \ldots, N_{p}
\]

\[
\sum_{i=1}^{N_{p}} n_{i} T_{Li} \leq H
\]

Objective function

Sizing

Process time

Demand

Horizon time

Disjunction for Task Assignments

Nonconvex functions
GDP model (continued)

\[ YEX_j = \frac{\gamma_j + \alpha V_j^{0.8}}{V_j^{L}} \leq V_j \leq V_j^{U} \]

\[
\begin{bmatrix}
Y_{C_{1j}} \\
N_{j}^{eq} = 1 \\
T_{i_j} \geq p_{i_q}
\end{bmatrix} \lor 
\begin{bmatrix}
Y_{C_{2j}} \\
N_{j}^{eq} = 2 \\
2T_{i_j} \geq p_{i_q}
\end{bmatrix} \lor 
\begin{bmatrix}
Y_{C_{3j}} \\
N_{j}^{eq} = 3 \\
3T_{i_j} \geq p_{i_q}
\end{bmatrix} \lor 
\begin{bmatrix}
Y_{C_{4j}} \\
N_{j}^{eq} = 4 \\
4T_{i_j} \geq p_{i_q}
\end{bmatrix}
\]

\[ \neg YEX_j \]

\[
\begin{bmatrix}
C_j = 0 \\
V_j = 0 \\
N_{j}^{eq} = 0 \\
pt_{i_q} = 0 \\
T_{i_j} \geq 0
\end{bmatrix}
\]

\[ j \in J \]

**Disjunction for Equipment**

**Disjunction for Storage Tank**

\[ CS_j = 5000 + 80VST_j^{0.5} \]

\[ YEX_1 \iff Y_{i_1}, X_2 \iff Y_{i_2} \lor Y_{i_3}, \ldots, YEX_5 \iff Y_{i_5} \]

\[ W_{0i} \lor W_{1i} \lor W_{2i} \lor W_{3i} \]

\[ W_{0i} \iff \neg Y_{i_4} \land \neg Y_{i_2} \land \neg Y_{i_3} \]

\[ W_{14} \iff (Y_{i_4} \land \neg Y_{i_2} \land \neg Y_{i_3}) \lor (\neg Y_{i_4} \land Y_{i_2} \land \neg Y_{i_3}) \lor (\neg Y_{i_4} \land \neg Y_{i_2} \land Y_{i_3}) \]

\[ W_{24} \iff (Y_{i_4} \land Y_{i_2} \land \neg Y_{i_3}) \lor (\neg Y_{i_4} \land Y_{i_2} \land Y_{i_3}) \]

\[ W_{34} \iff Y_{i_4} \land Y_{i_2} \land Y_{i_3} \]

\[ 0 \leq C_j, V_j, V_j^+, n_j, B_j, T_{i_j}, p_{i_q}, N_{j}^{eq}, p_{t_q} \]

\[ YEX_q, Y_q, YC_q, W_q \in \{true, false\} \]

**Logic Propositions**

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Proposed Algorithm for Nonconvex GDP

Step 0
- Nonconvex MINLP
  \[ Z^U \]

OA (Viswanathan and Grossmann, 1990)

Step 1
- Bound Contraction
  \[ \text{New Bound} \]

(Zamora and Grossmann, 1999)

Step 2
- BB with Y’s Update \( Z^L \)
  \[ \text{Stop when } Z^L \geq Z^U \]
- When solution is Integral
- Add Integer Cut

(Lee and Grossmann, 2000)

Step 3
- Spatial BB Update \( Z^U \)
- Fixed Y’s

(Quesada and Grossmann, 1995)

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Step 2: Disjunctive Branch and Bound

- **Procedure** (Lee and Grossmann, 1999)
  - Relaxed NLP problem is solved.
  - Check Infeasibility of each term.

- **Branching Rule**
  - Select a term with Minimum Infeasibility first.
  - Logic Inference – fixes additional Boolean Variables.

- **Lower Bound is updated**

- When all the Boolean variables are fixed and the relaxation gap is nonzero:
  - switch to Spatial Branch and Bound.
Step 3: Spatial Branch and Bound

- **Fixed Boolean Variables: Convex NLP**
  - Check the relaxation gap of each underestimator function.
  - Select the constraint with maximum gap.
  - Branch on a variable which causes the maximum gap.
  - Bisection Rule: Feasible region is divided into 2 subregions.
  - If the gap is small enough, an upper bound is updated.

- **Return to Step 2 with:**
  - Updated Global Upper Bound
  - Feasibility Cut, $Z < \text{GUB}$
  - Integer Cut for the chosen set of Y’s

Quesada and Grossmann (1995)

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Upper Bound Solution

Cost = $277,928 (by GAMS/DICOPT++)

- Use 4 Stages (6 units) without Storage Tank

**Mixing**

- \( V_1 = 4,842 \text{ L} \)

**Reaction**

- \( V_2 = 2,881 \text{ L} \)

**Crystallization**

- \( V_4 = 2,469 \text{ L} \)

**Drying**

- \( V_5 = 8,071 \text{ L} \)

A 243 batches, 4.5hrs

B 260 batches, 6hrs

C 372 batches, 9hrs

6000 hrs

1093 hrs

1562 hrs

3345 hrs

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Optimal Solution: Multiproduct Batch Plant

- Global optimal cost = $264,887 (5% improvement)
- 3 Stages + 1 storage tank (5 units)

V_2 = 4,309 L  \quad VST_2 = 4,800 L  \quad V_3 = 3,600 L  \quad V_5 = 11,753 L

Storage 1503 hrs  2202 hrs  2295 hrs

6000 hrs

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Environmentally Conscious Design and Planning of Hydrogen Supply Chains for Vehicle Use

Guillén-Gosálbez, Mele and Grossmann (2009)

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

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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-gaseous 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

\[ \text{Min Cost} \]
\[ \text{Min Environmental impact} \]

s.t. Mass balances (defined for every grid)
Capacity constraints (production and storage)
Capacity constraints (transportation)
0-1 vars choices, cont vars flows
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

Environmental aspects based on LCA (Eco-Indicator 99)

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)

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

   • Human health: DALYs (Disability Adjusted Life Years)

\[
DAM = \sum_b \nu_b LCI_b
\]

Damage factors translate life cycle inventory into impact
Solution strategy: Epsilon constraint

Bi-criterion MILP with economic and environmental concerns

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

Pareto-optimal solutions: Epsilon constraint method

Solve a set of single objective problems for different values of \( \varepsilon \)

\[
\begin{align*}
\min_{x, X, N} & \quad (\text{TDC}(x, X, N)) \\
\text{s.t.} & \quad g(x, X, N) \leq 0 \\
& \quad h(x, X, N) = 0 \\
& \quad \text{DAM}(x, X, N) \leq \varepsilon \\
& \quad \underline{\varepsilon} \leq \varepsilon \leq \bar{\varepsilon} \\
& \quad x \in \mathbb{R}, X \in \{0, 1\}, N \in \mathbb{N}
\end{align*}
\]
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 centralized network (economies of scale)

MINIMUM IMPACT: more decentralized network (reduces transportation emissions)
Concluding Remarks

1. Process synthesis: challenging problem that lies at heart of design and that is key to address sustainability problems

2. Process synthesis has greatly advanced in representations and optimization methodologies

3. Advances in mixed-integer/disjunctive programming have provided a powerful framework for addressing synthesis problems

4. Many problems can be effectively addressed
   *HENs, Water networks, steam and power plants, separations systems*  
   *Process flowsheets*

5. Challenges: *uncertainty, process intensification, nonliner modeling*