Sustainable Process Synthesis and Intensification for Industrial Decarbonization

Faruque Hasan, PhD

Artie McFerrin Department of Chemical Engineering, Texas A&M University
College Station, TX, USA

ARTIE MCFERRIN DEPARTMENT OF CHEMICAL ENGINEERING TEXAS A&M UNIVERSITY

TEXAS A&M UNIVERSITY Texas A&M Energy Institute

TEES Texas A&M Engineering Experiment Station

2022 Seminar for Energy Systems Initiative (ESI) at the Center for Advanced Process Decision-Making (CAPD)
November 09, 2022

Chemical Process Industry (CPI)

Meets the societal demands for chemicals and commodity products

Raw materials

Fossil fuels (**coal**, **natural gas**, and **petroleum**), air, water, salt, limestone, **sulfur** or an equivalent, and some specialized raw materials.

Chemical enterprises

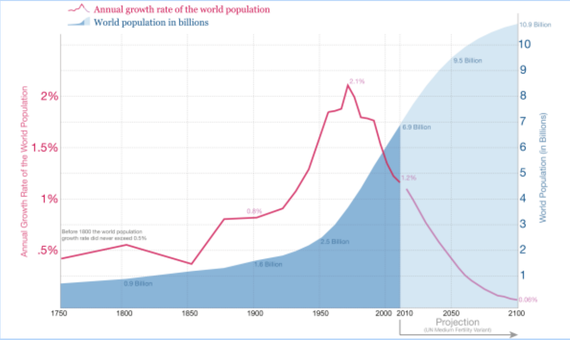
Products

- In 2017, the chemical industry contributed **$5.7 trillion** to global GDP
- In 2018, **top 50 chemical companies**, excluding PetroChina, had a combined chemical revenue of **$926.8 billion** (C&EN, July 2019)

Global Challenges

Increasing demand

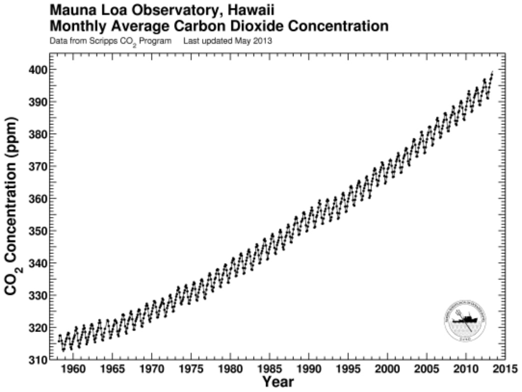
World population growth, 1750-2100

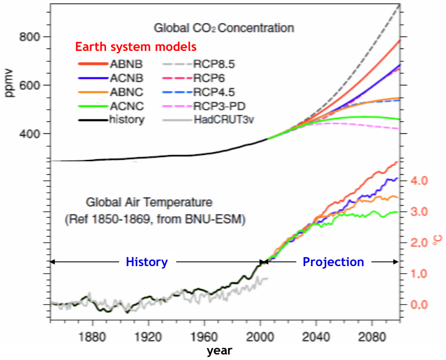


Increase in water, energy & commodities demand

6-7 x	Global GDP growth over next ~50 years (in constant dollars)	
5-6 x	Production capacity for most commodities (steel, chemicals, lumber, etc.)	
3.5 x	Energy demand	7 x Electricity demand
Increase	Water demand	

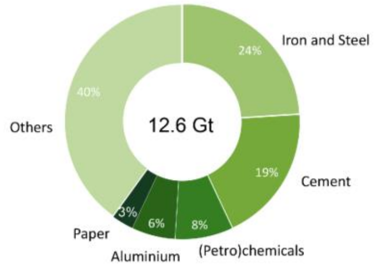
Increasing emission





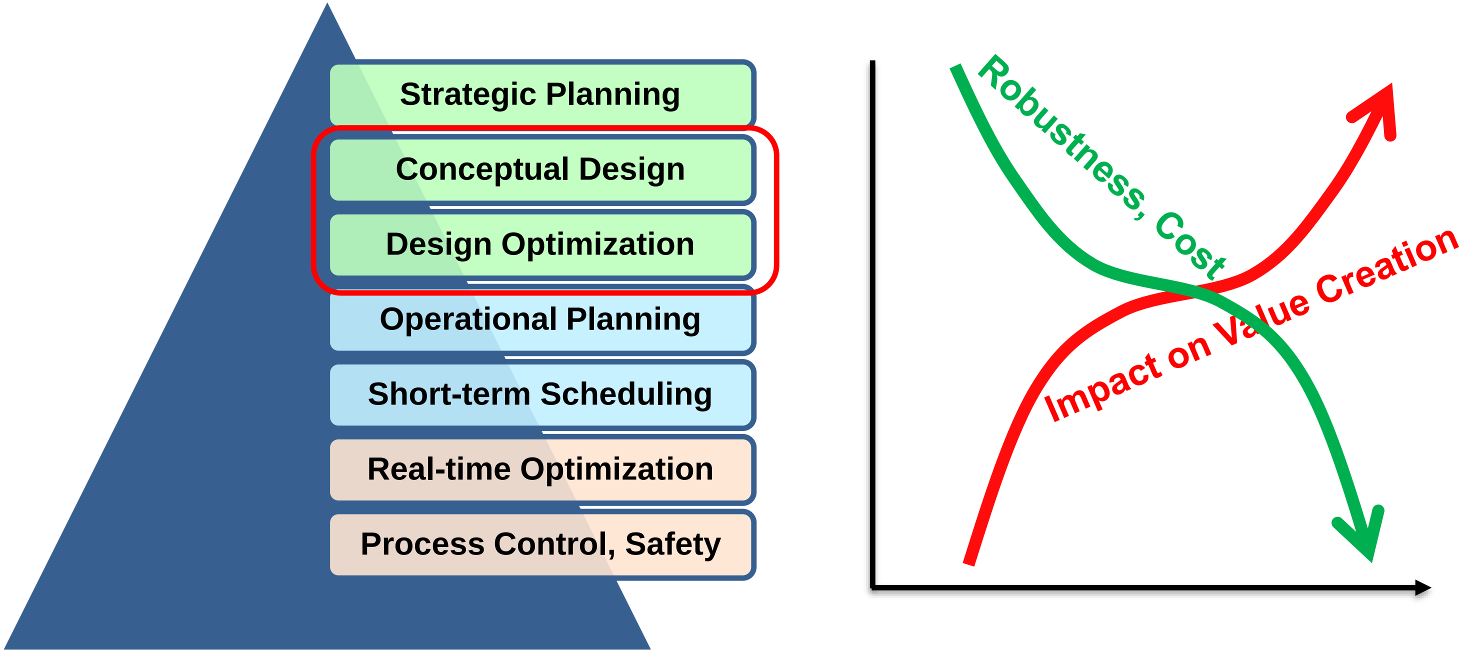
Wei *et al.*, *PNAS*, 2012, 109(32), 12911-12915

Global CO2 emissions from industry: key sectors

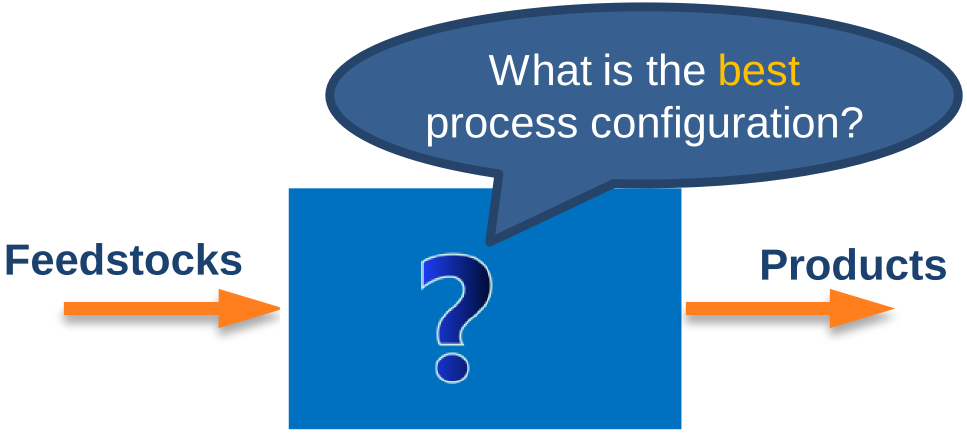


Source: World Economic Forum

Process Systems Engineering Opportunities



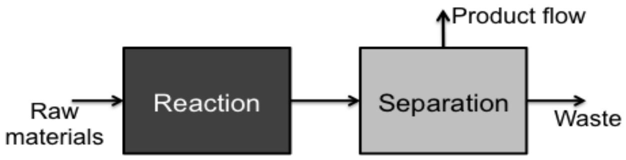
Fundamental Questions in Process Design



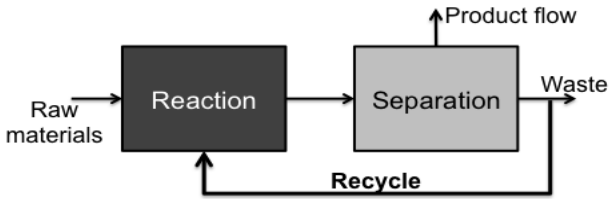
- Feasibility
    - product quality, demand
- Optimality
    - Cost, energy consumption, waste, emission
    - Profit, NPV, ROI
- Operability, flexibility
- Sustainability, circularity
- Safety

Pillars of Process Design

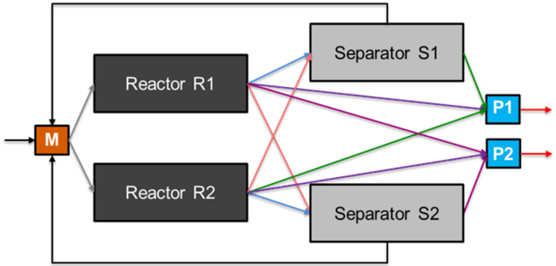
Conceptual Design



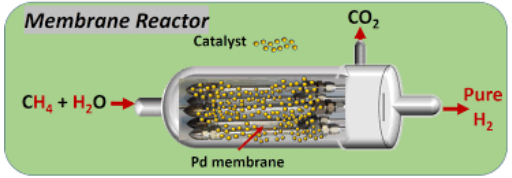
Process Integration



Process Synthesis



Process Intensification

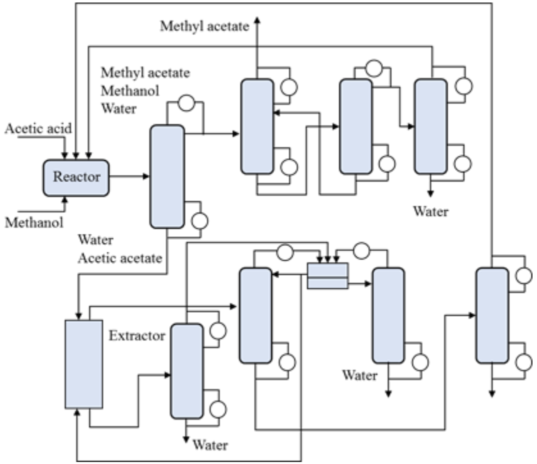


Intensification can be viewed as an extreme case of integration (Baldea, 2015)

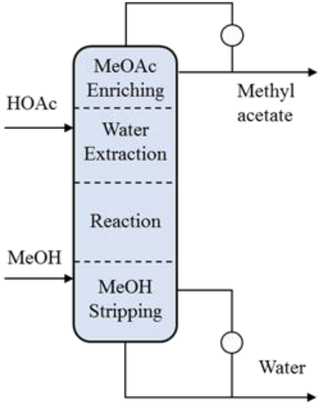
Process Intensification

- Synergistic combination of multiple phenomena and tasks to achieve drastic improvement
- Examples include reactive distillation, membrane reactors, dividing wall columns

Conventional Proceess



Eastman Chemical Task-integrated Column

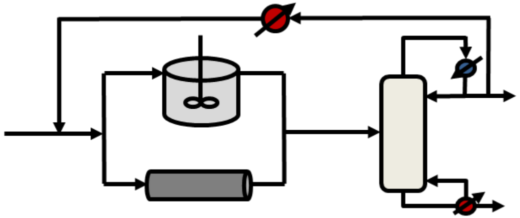


Computer-aided Process Intensification

- Synthesis
  - How can we systematically discover innovative and intensified process systems without waiting for “eureka moments”?
- Identification
  - How can we systematically identify intensification pathways or “intensification hotspots”?
- Analysis
  - Under what conditions is intensification desirable?
  - Can we measure intensifiability? How?
  - Which phenomena should be intensified?

Representation is fundamental to systematic process innovation

Representation Methods



Superstructure Representation

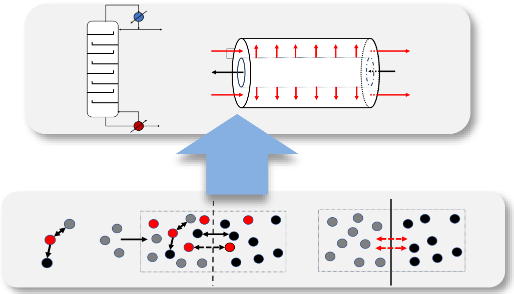
Optimization-based Process Synthesis

Systematic screening of alternatives (Mencareli, Chen, Pagot, Grossmann, Compute. Chem. Eng., 2020, 136, 106808)

- Postulate a process superstructure (e.g., P-graph, STN, SEN, UPCS, etc.) and formulate a mathematical program
- Use optimization algorithm to search configurations

Unit operation Focus

Unit operations



Physicochemical Phenomena

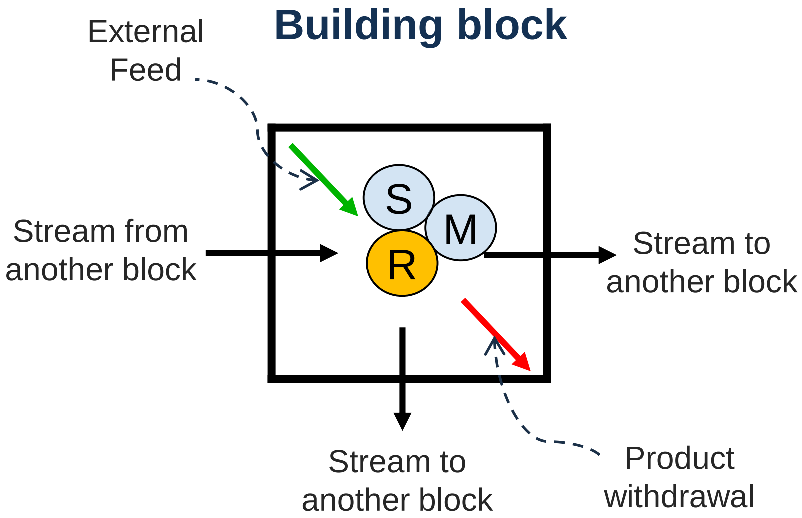
Phenomena/Functional/Modular Approaches

- **Phenomena Building Blocks (PBB)**
  - Lutze et al., 2010; Babi et al., 2014; Tula et al., 2017
- **Generalized Modular Framework (GMF)**
  - Papalexandri and Pistikopoulos, 1996; Tian et al. 2018
- **IDEAS Approach and State-space Representation**
  - Wilson and Manousiouthakis, 2000; Cruz and Manousiouthakis, 2017
- **Functional modules**
  - Freund and Sundmacher, 2008; Kaiser et al., 2018

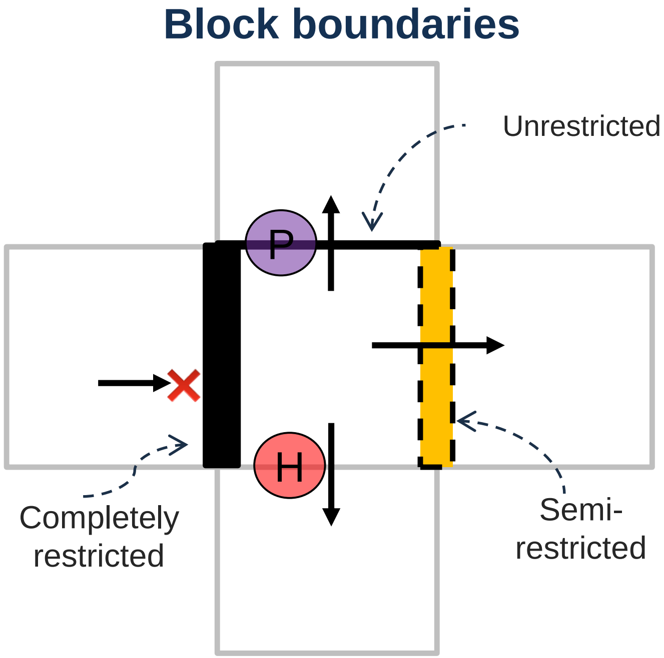
Departure from Unit Operation Focus

Representation using Design Building Blocks

Demirel, Li and Hasan, *Compute. Chem. Eng.*, 2017

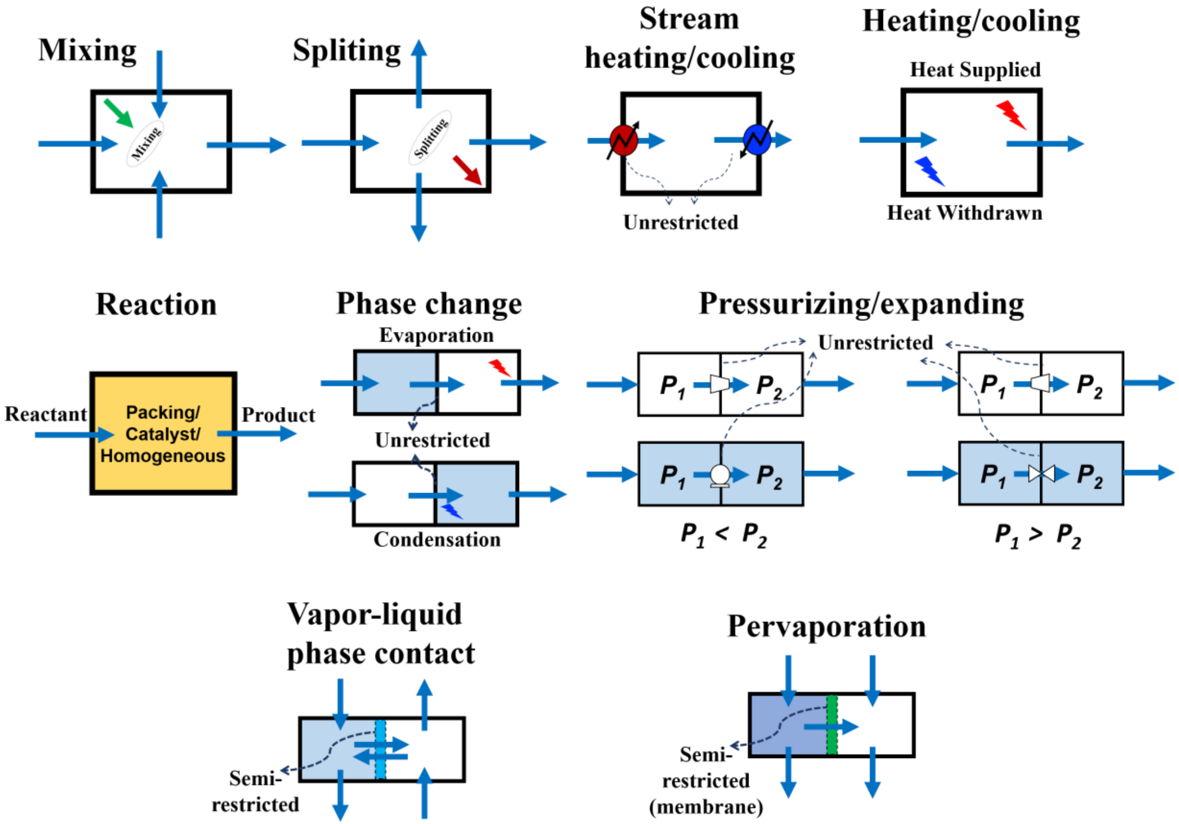


Physical Attributes: Temperature, Pressure, Composition
A unit use of a material (e.g. catalyst)



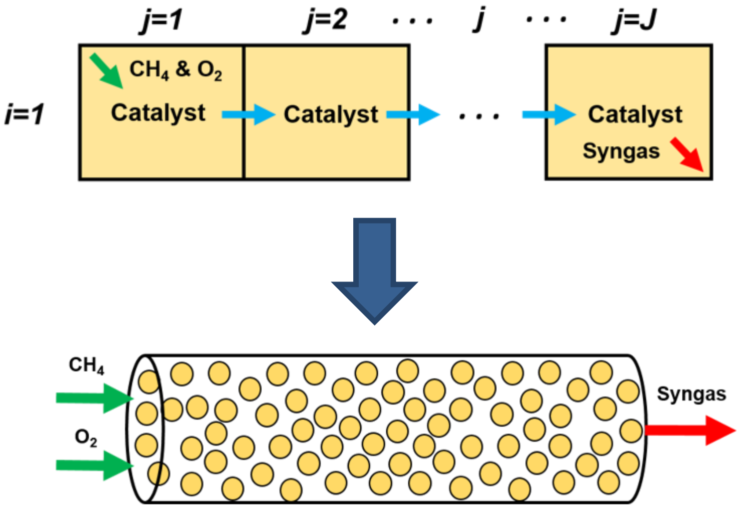
3 types of Building Block Boundaries

Phenomena Representation



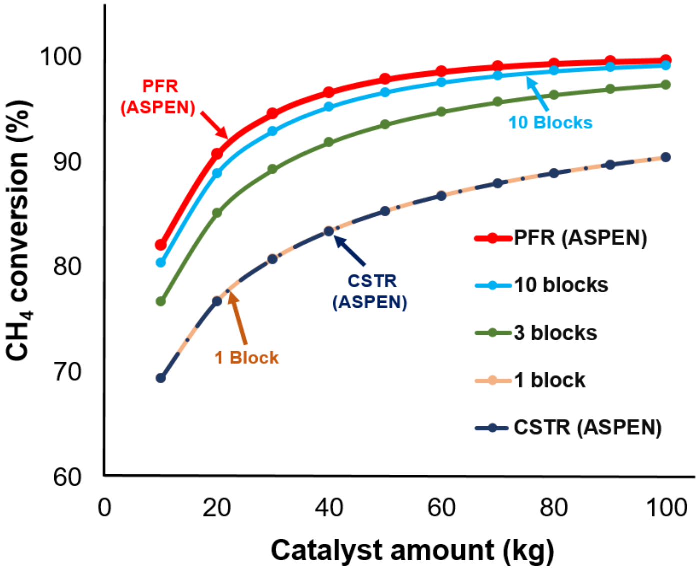
Building Blocks to Phenomena to Unit Operations

CSTR

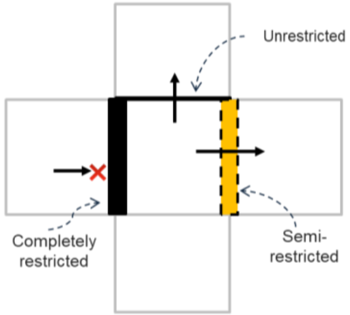


Plug Flow Reactor (PFR)

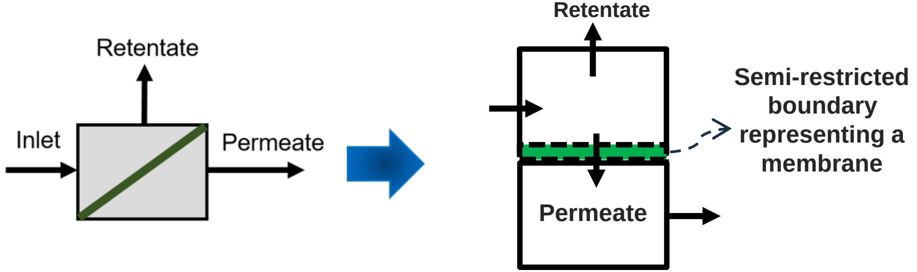
Methane partial oxidation (POX)
(De Groote and Froment, 1996)

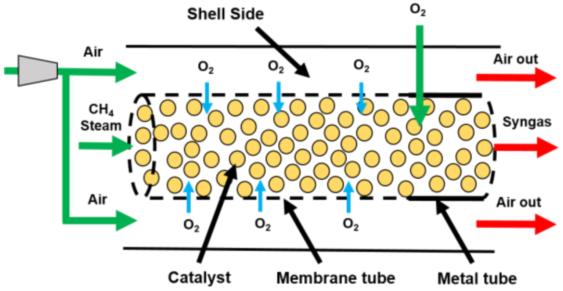


Building Blocks to Phenomena to Unit Operations

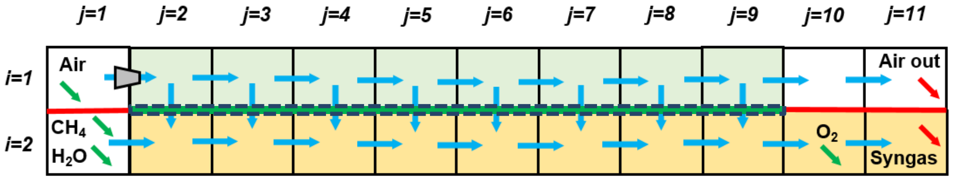


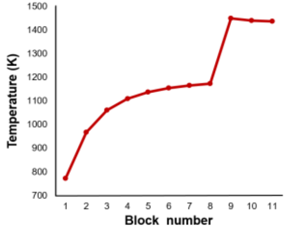
Membrane separator

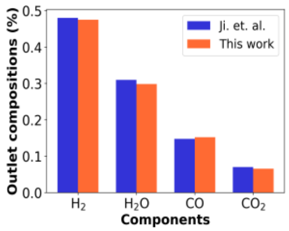


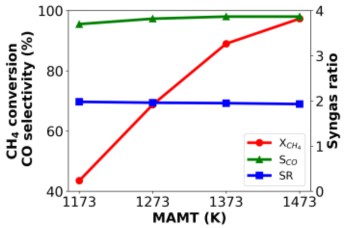


Partially intensified side-feed membrane reactor



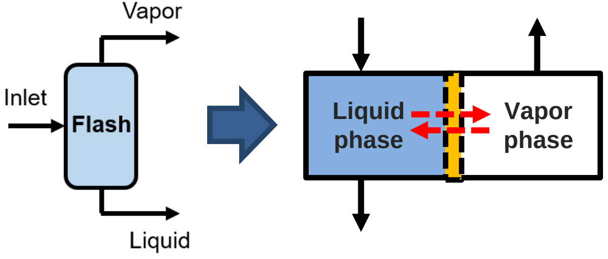




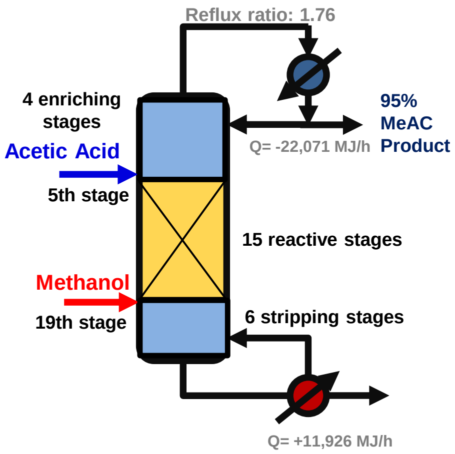


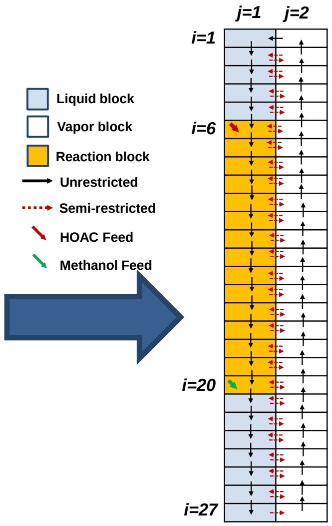
Building Blocks to Phenomena to Unit Operations

Flash separator

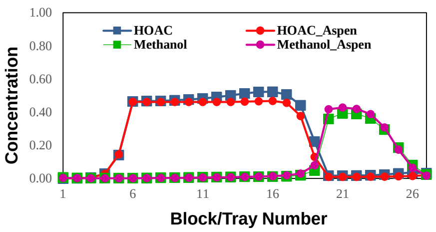


Eastman Chemical task-integrated column

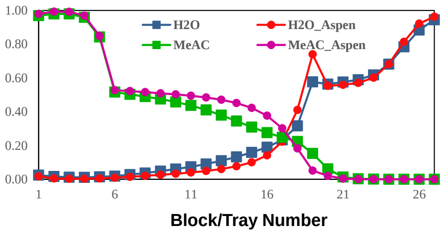




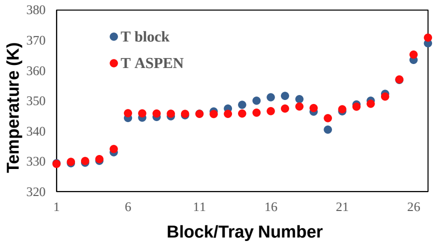
Liquid Mole fraction (Reactants)



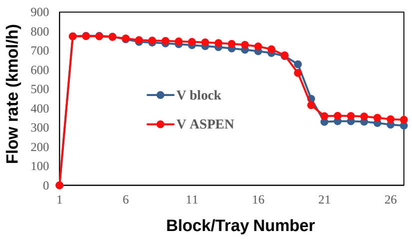
Liquid Mole fraction (Products)



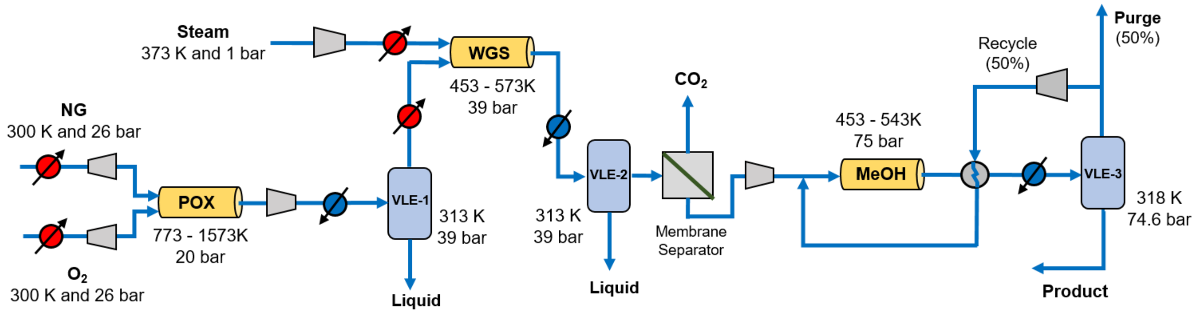
Temperature Profile



Vapor Flow Rate

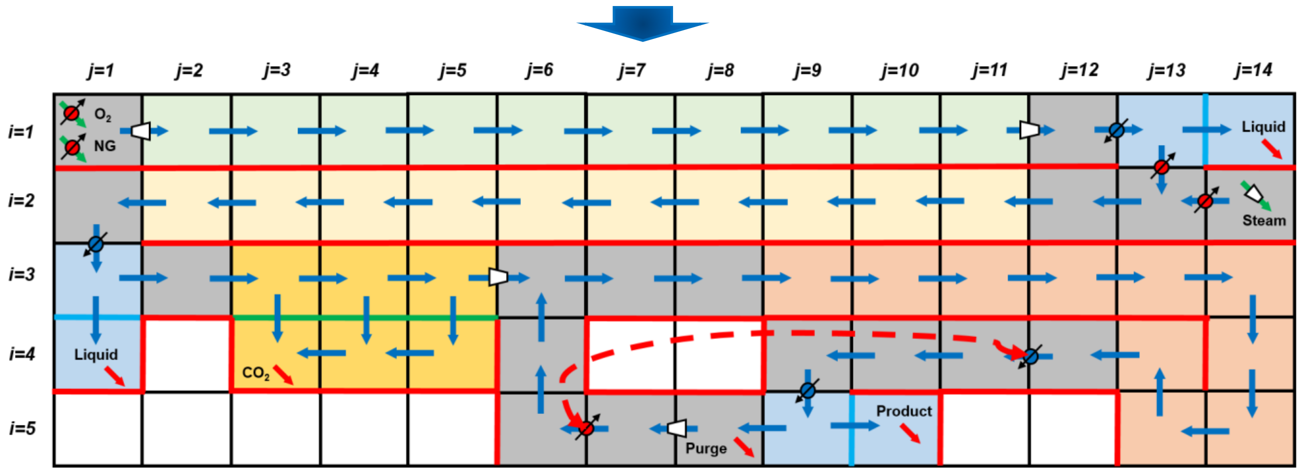


Process Flowsheet Representation

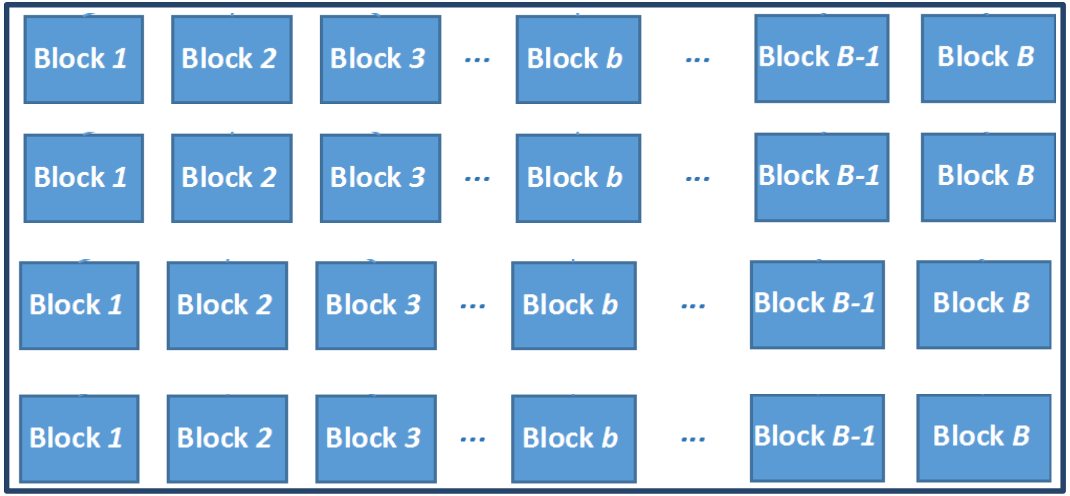


Base Case:

ROI: 38%

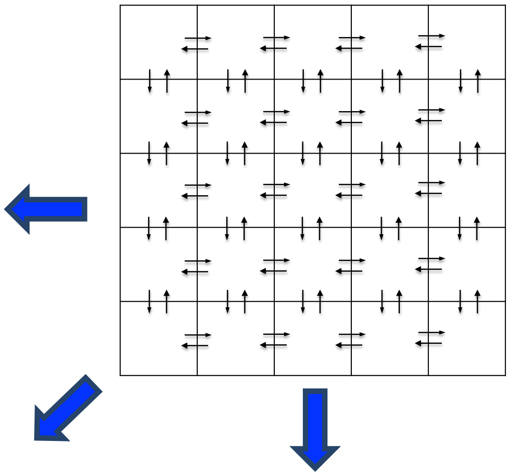


A General Representation for Process Synthesis and Intensification

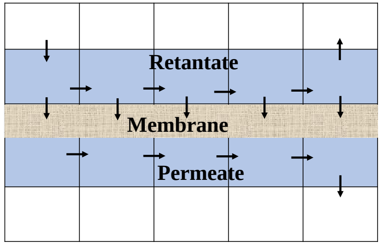


Intensified Equipment Alternatives

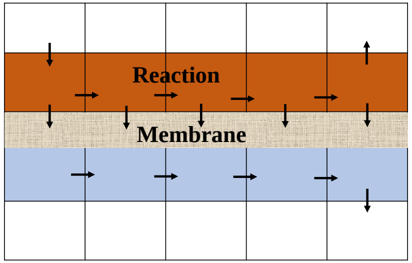
Building Block Superstructure



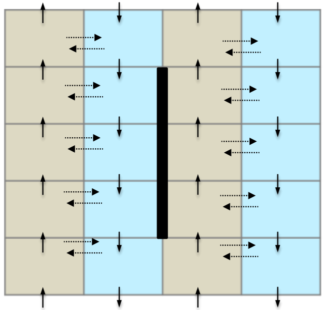
a) Gas Separation Membrane



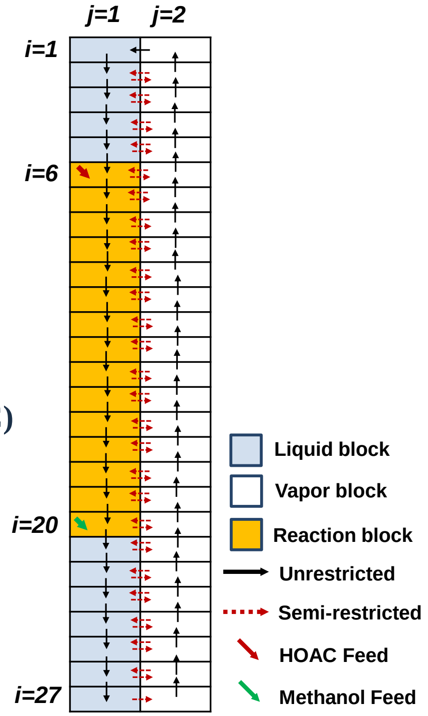
b) Membrane Reactor



c) Dividing Wall Column Distillation (DWC)



d) Eastman Chemical Methyl Acetate Column



Mathematical Model Formulation

Given: Process Feed; Product purity and recovery; Material properties; Physicochemical data

$$MIN \quad f(\boldsymbol{x}, \boldsymbol{z})$$

$$s.t.$$

$$h_t(\boldsymbol{x}) = 0 \qquad \forall t = 1, \cdots, T$$

$$g_q(\boldsymbol{z}) \leq 0 \qquad \forall q = 1, \cdots, Q$$

$$g_l(\boldsymbol{x}, \boldsymbol{z}) \leq 0 \qquad \forall q = 1, \cdots, L$$

$$\boldsymbol{x}^L \leq \boldsymbol{x} \leq \boldsymbol{x}^U \quad \boldsymbol{x} \in R^{I \times J \times K}$$

$$z = \{0,1\}^s$$

Objective: Maximize annual profit, product yield; Minimize cost, utility, total volume, etc.

Balance constraints:
Material and Energy balances

Assignment Constraints:
Phenomena and material assignments and Phase Determination

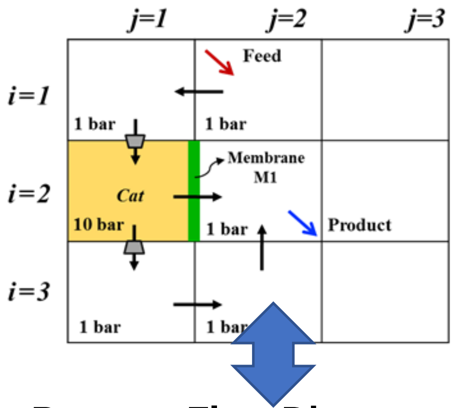
Logical Constraints:
Relating discrete variables with the continuous variables. These also includes phenomena models (rigorous/short-cut/high-level).

***x*: Continous mass and energy flow variables**

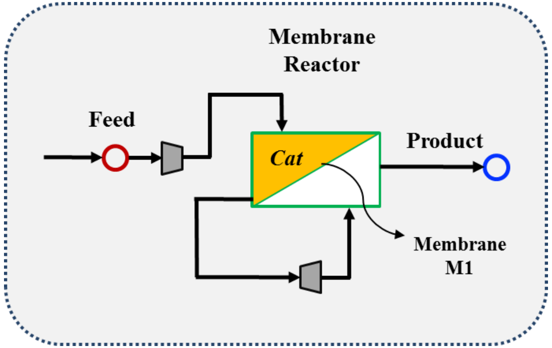
***z*: binary variables for assigning phenomena, boundaries and functional materials**

Transition from Building Blocks to PFDs

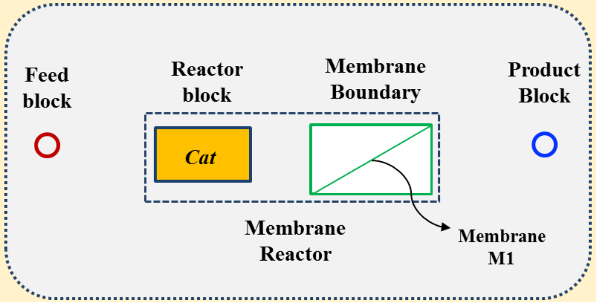
Block Superstructure Result



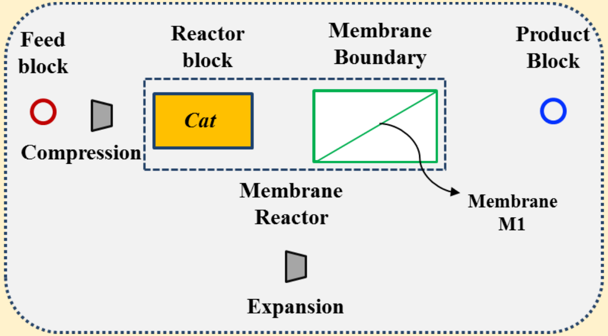
Process Flow Diagram



Identification of Major Operations

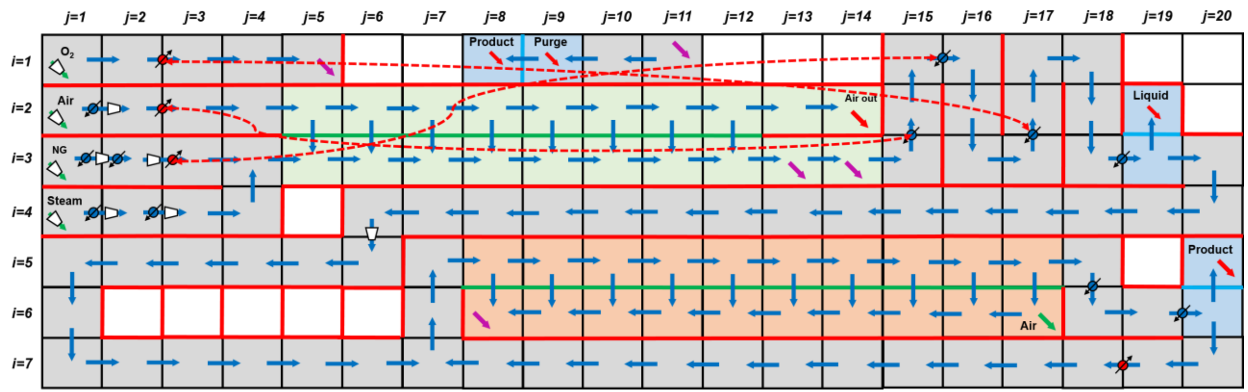


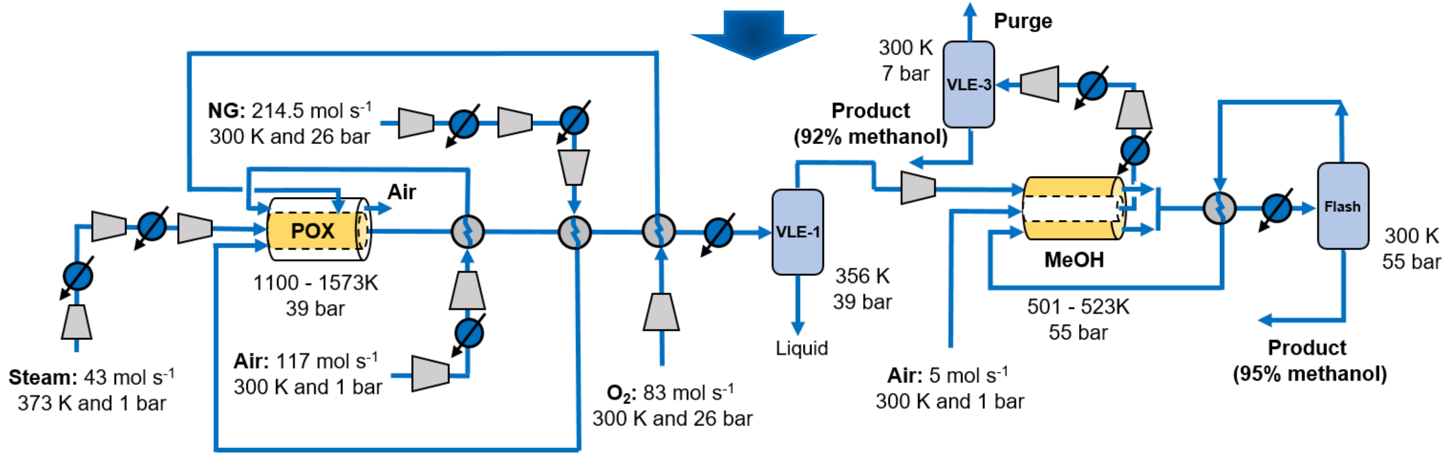
Identification of Auxiliary Operations



Process Synthesis

Monjur and Hasan, AIChE J., 2022





ROI: 52%

SPICE Framework

User Inputs
- Feedstocks, products and utility specifications (compositions, flow rates, *T*, *P*)
- Design targets (purity, product demands, emission, specific considerations, etc.)

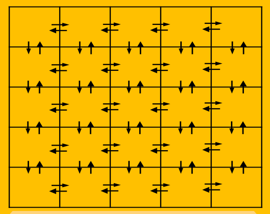
Material Library
- Reaction library (type, density, porosity, catalyst, kinetics, stoichiometry, selectivity)
- Membrane library (type, permeance, selectivity)
- User defined data, if any

Techno-Economic and Life Cycle Data
- Cost functions and economic parameters (scaling factors, plant life, depreciation, annualizing factor, utility costs, fixed costs, etc.)
- Equipment sizing data
- Emission parameters

Target Representations
- Phenomenal or task level
- Unit operations level
- Flowsheet and process network levels

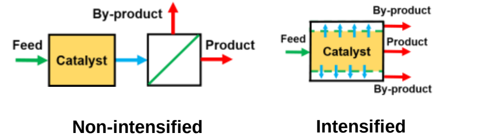
SPICE

(Synthesis and Process Intensification of Chemical Processes)

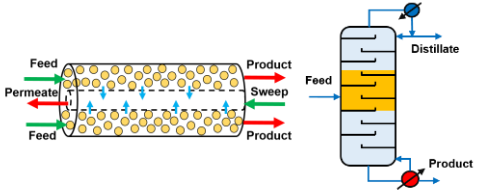


Building block representation	Thermodynamic property models
Material and energy balances	Phenomena models
Equilibrium, kinetic and transport models	Objective functions

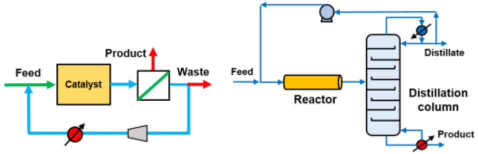
Targeting, Conceptual Design, and Benchmarking
- Non-intensified equipment
- Intensified equipment



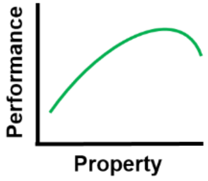
Process Library
- Automated generation of intensified equipment configurations and process flow diagrams (PFDs)
- Simulation, sensitivity analysis, TEA, LCA



Process Synthesis and Optimization
- Automated screening of process networks
- Design optimization, and sustainability
- Simultaneous heat integration

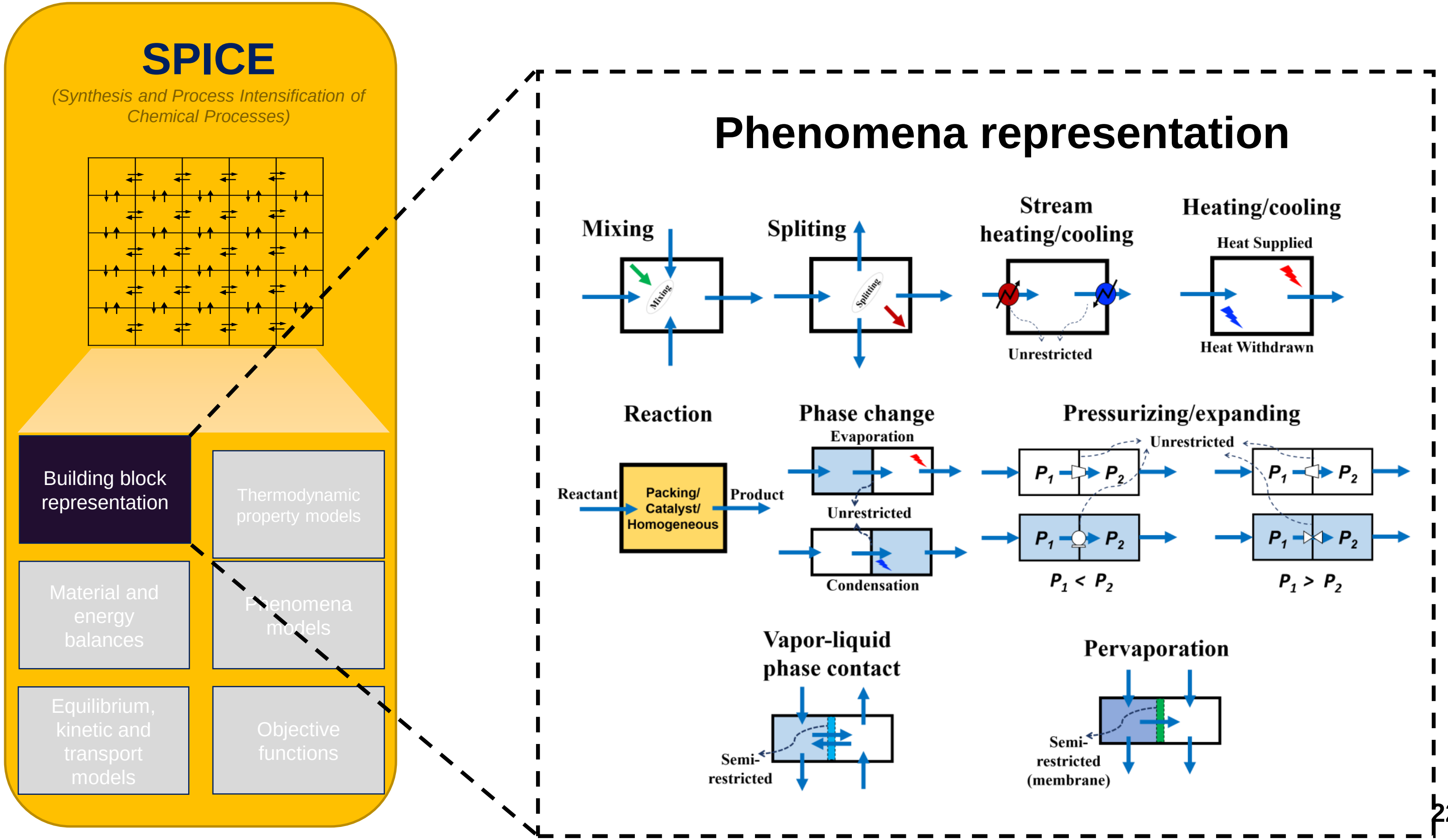


Material-Property-Performance Mapping



Demirel et al, 2017, 2019 and Li et. al. 2018

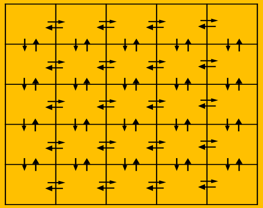
Building Block Representation



Model Formulation

SPICE

(Synthesis and Process Intensification of Chemical Processes)



- Building block representation
- Thermodynamic property models
- Material and energy balances
- Phenomena models
- Equilibrium, kinetic and transport models
- Objective functions

Given: Process Feed; Product purity and recovery; Material properties; Physicochemical data

Objective: Maximize annual profit, product yield; Minimize cost, utility, total volume, etc.

$$MIN \quad f(\boldsymbol{x}, \boldsymbol{z})$$

$s.t.$

$$h_t(\boldsymbol{x}) = 0 \qquad \forall t = 1, \cdots, T$$

$$g_q(\boldsymbol{z}) \leq 0 \qquad \forall q = 1, \cdots, Q$$

$$g_l(\boldsymbol{x}, \boldsymbol{z}) \leq 0 \qquad \forall q = 1, \cdots, L$$

$$\boldsymbol{x}^L \leq \boldsymbol{x} \leq \boldsymbol{x}^U \quad \boldsymbol{x} \in R^{I \times J \times K}$$

$$z = \{0,1\}^s$$

Balance constraints: Material and Energy balances

Assignment Constraints: Phenomena and material assignments and Phase Determination

Logical Constraints: Relating discrete variables with the continuous variables. These also includes phenomena models (rigorous/short-cut/high-level).

x: Continous mass and energy flow variables

z: binary variables for assigning phenomena, boundaries and functional materials

Material balance around each block:

$$F_{i,j-1,k} - F_{i,j,k} + R_{i-1,j,k} - R_{i,j,k} + G_{i,j,k} + \sum_{f \in FS} M_{i,j,k,f} - \sum_{p \in PS} P_{i,j,k,p} = 0$$

Reaction phenomena model:

$$G_{i,j,k} = \sum_{r \in R, c \in CAT} f(T_{i,j}, P_{i,j}, y_{i,j,k}, k_{i,j,r,c}) \qquad k_{i,j,r,c} = f^{rxn}(T_{i,j}, P_{i,j}, y_{i,j,k}, k_{i,j,r,c})$$

Energy balance around each block:

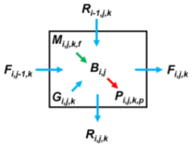
$$EF_{i,j-1} - EF_{i,j} + ER_{i-1,j} - ER_{i,j} + EG_{i,j} + EM_{i,j} - EP_{i,j} + Q_{i,j} + W_{i,j} = 0$$

Separation phenomena model:

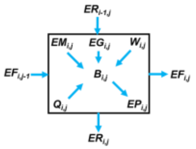
$$F_{i,j,k,1} = f(T_{i,j}, P_{i,j}, y_{i,j,k}, T_{i,j+1}, P_{i,j+1}, y_{i,j+1,k})$$

Minimize total annual cost (TAC)

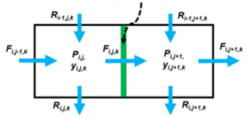
$$min \quad TAC = \sum_{i \in I} \sum_{j \in J} \sum_{k \in K} UC^f M_{i,j,k,f} + UC^{EL} \sum_{i \in I} \sum_{j \in J} W_{i,j}^{comp} + UC^{CU} \sum_{i \in I} \sum_{j \in J} Q_{i,j}^c + UC^{HU} \sum_{i \in I} \sum_{j \in J} Q_{i,j}^h + \gamma_a \sum_{e \in E} C_e \left(\frac{S_e}{S_e^{ref}} \right)^{n_e}$$



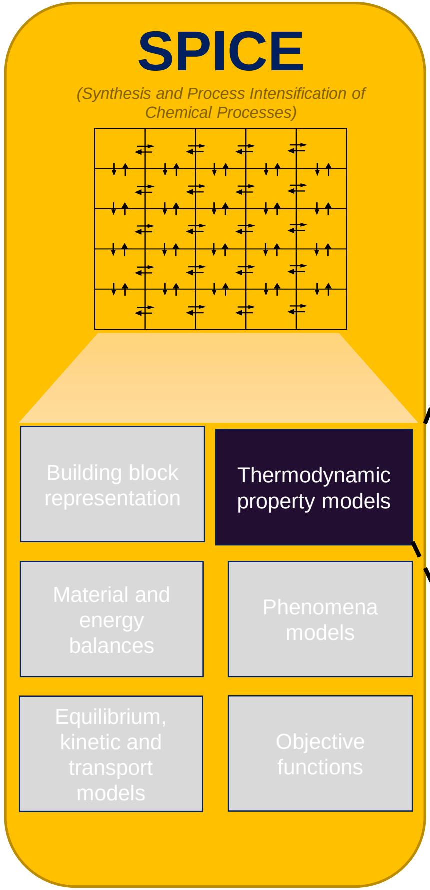
Material Flow Variables



Energy Flow Variables

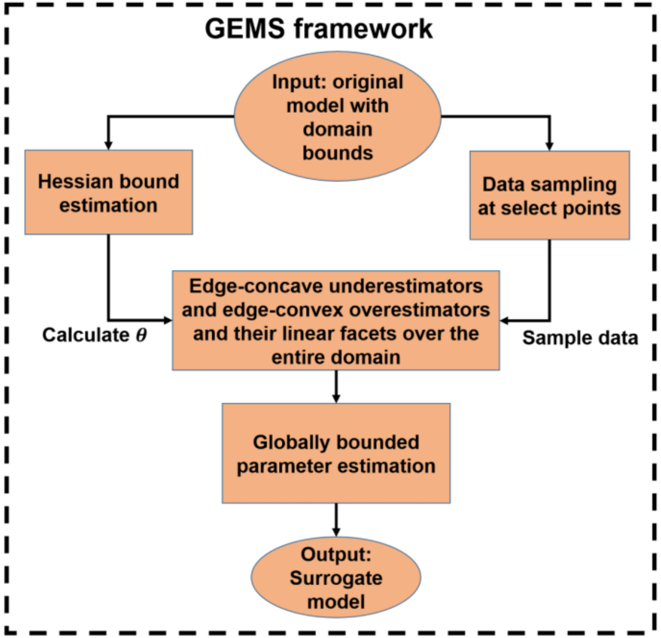


Thermodynamic Models



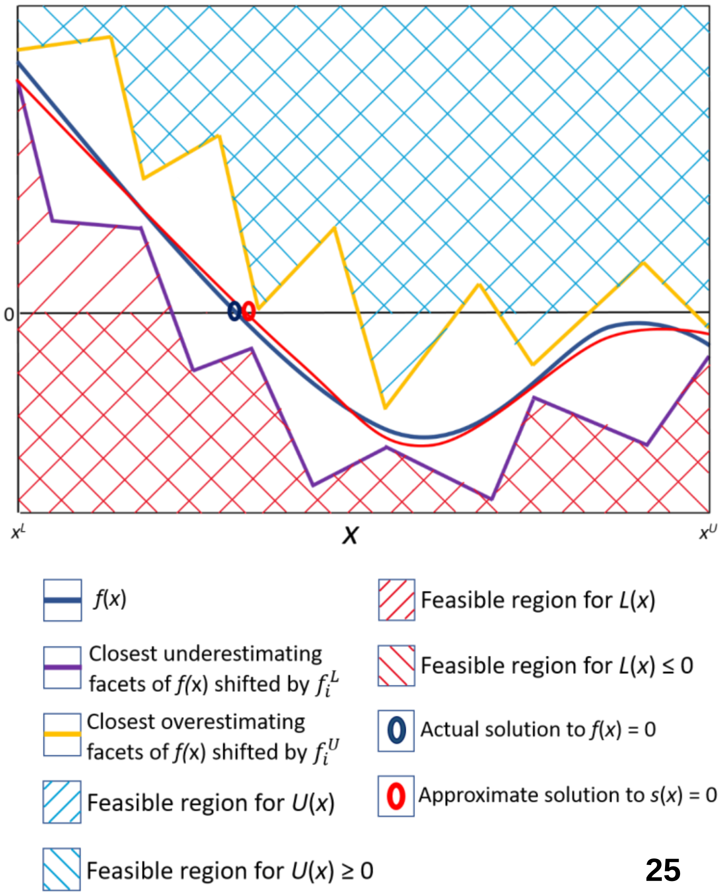
GEMS (Guaranteed Error-bounded Surrogate Modeling)

prescribed error-bounded outputs, even though based on model based sampling

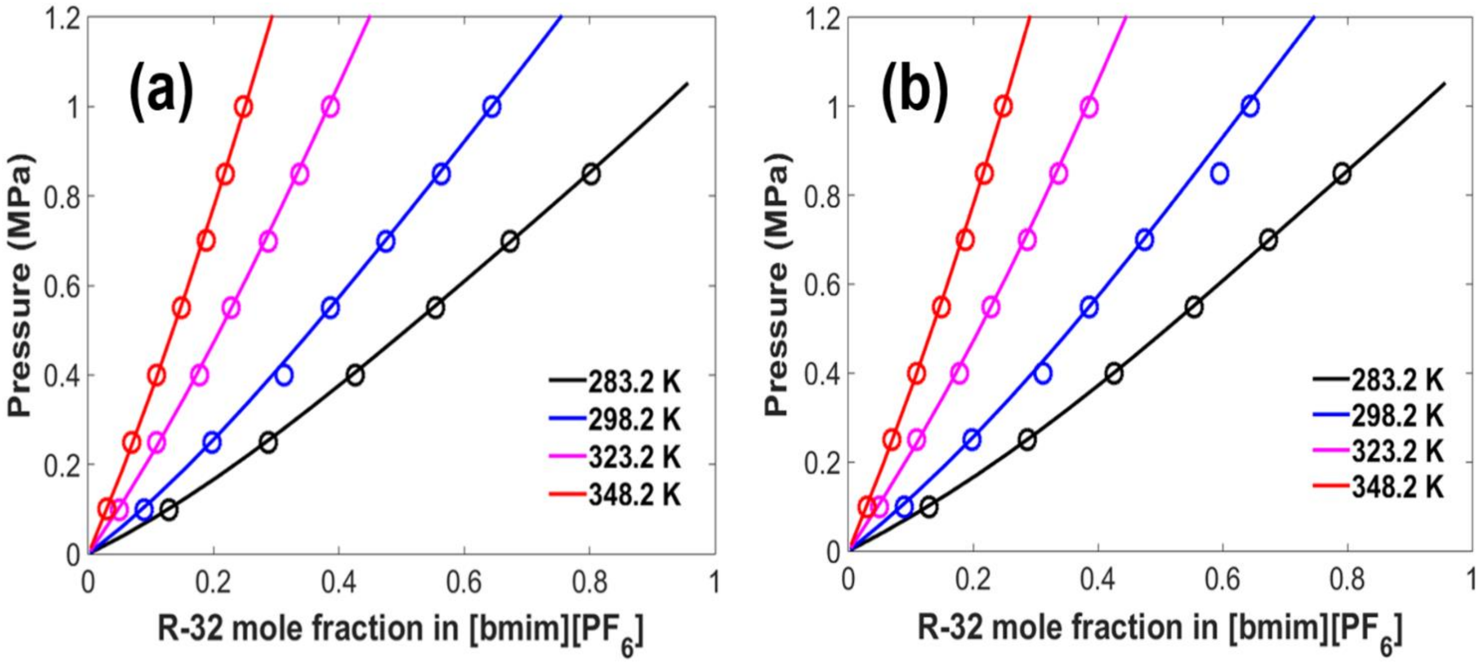


Error Bounded surrogate model parameter estimation: NLP Formulation

$\min \sum_{n=1}^{N}\left[\left(\frac{\hat{f}_i - s_i}{\hat{f}_i}\right)^2 + \left(\frac{f_i^U - \hat{f}_i}{\hat{f}_i}\right)^2 + \left(\frac{\hat{f}_i - f_i^L}{\hat{f}_i}\right)^2\right]$	**Objective function**
$s_i = \alpha + \sum_{n=1}^{N} \beta_n \hat{x}_{i,n} + \sum_{n=1}^{N}\sum_{m=n}^{N} \gamma_{n,m}\hat{x}_{i,n}\hat{x}_{i,m}$	**Surrogate form**
$f_i^L - \sum_{n=1}^{N} \theta_n^{f,L} \cdot \left(x_{i,n,v} - x_{i,n}^{int}\right)^2 - \sum_{n=1}^{N} \theta_n^{s,L} \cdot \left(x_{i,n,v} - x_{i,n}^{int}\right)^2 = s_i$ $f_i^U + \sum_{n=1}^{N} \theta_n^{f,U} \cdot \left(x_{i,n,v} - x_{i,n}^{int}\right)^2 + \sum_{n=1}^{N} \theta_n^{s,U} \cdot \left(x_{i,n,v} - x_{i,n}^{int}\right)^2 = s_i$	**Error-bounding of surrogate**
$\theta_n^{s,L} \geq \gamma_{n,n}$ $\theta_n^{s,U} \geq -\gamma_{n,n}$	**Edge concavity of surrogate underestimators**



Solubility prediction

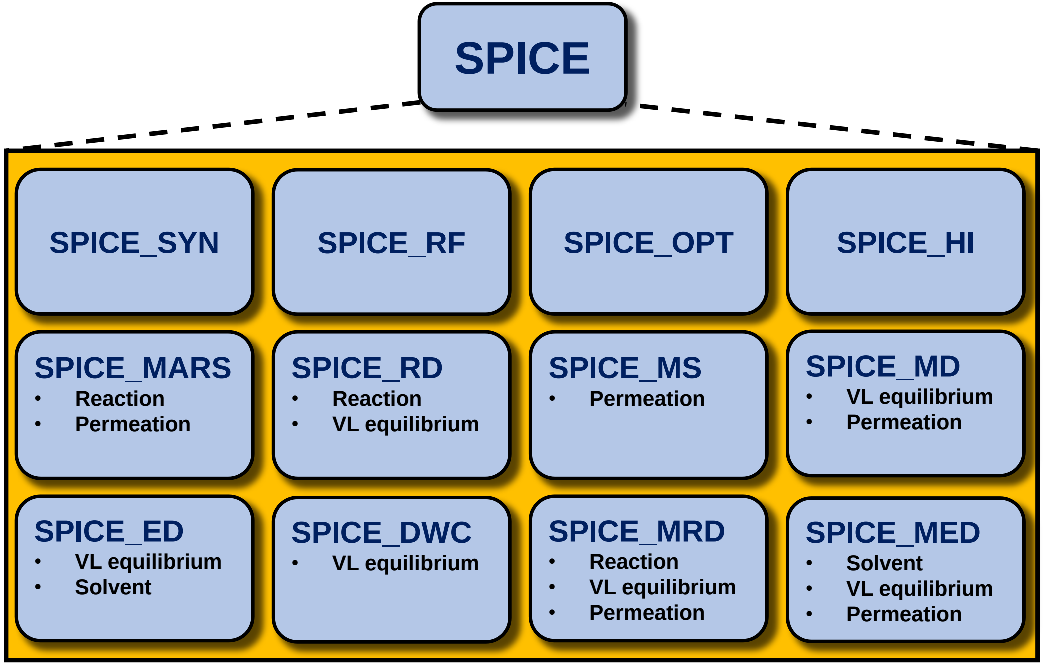


Iftakher et al., In *2022 American Control Conference (ACC)*, pp. 4814-4819. IEEE, 2022

Solid lines: Gamma-Phi model with (a) Margules activity coefficient, (b) NRTL activity coefficient

Circles: GEMS prediction

SPICE Suits



- Process Synthesis (SPICE_SYN)
- Retrofitting (SPICE_RF)
- Process Optimization (SPICE_OPT)
- Membrane Assisted Reactive Separations (SPICE_MARS)
- Reactive Distillation (SPICE_RD)
- Membrane Separation (SPICE_MS)
- Membrane Distillation (SPICE_MD)
- Extractive Distillation (SPICE_ED)
- Dividing Wall Column (SPICE_DWC)
- …
- …

Example: Intensification of Ethylene Glycol Production

Demirel, Li, El-Halwagi and Hasan, ACS Sus. Chem. Eng., 2020

Feed Streams:

- Ethylene Oxide (Sat'd Liquid)
- Water (Liquid at 298 K)

Reaction:

$$C_2H_4O + H_2O \rightarrow C_2H_6O_2$$

EthyleneOxide + Water → Ethylene Glycol

$$C_2H_4O + C_2H_6O_2 \rightarrow C_4H_{10}O_3$$

Ethylene Glycol + Etyhlene Oxide → Diethylene Glycol

- Liquid phase Homogeneous Reactions

$$r_1 = \exp\left(13.62 - \frac{8220}{T}\right) C_{EO}C_{H2O}$$

$$r_2 = \exp\left(15.57 - \frac{8700}{T}\right) C_{EO}C_{EG}$$

Target: 25 kmol/h EG production with 95% purity

Semiresticted Boundary (Separation Phenomena)

- Antoine equation for vapor pressure
- Ideal phase equilibrium
- ASPEN Plus parameters for density and vapor pressure

Maximize Return on Investment (ROI)

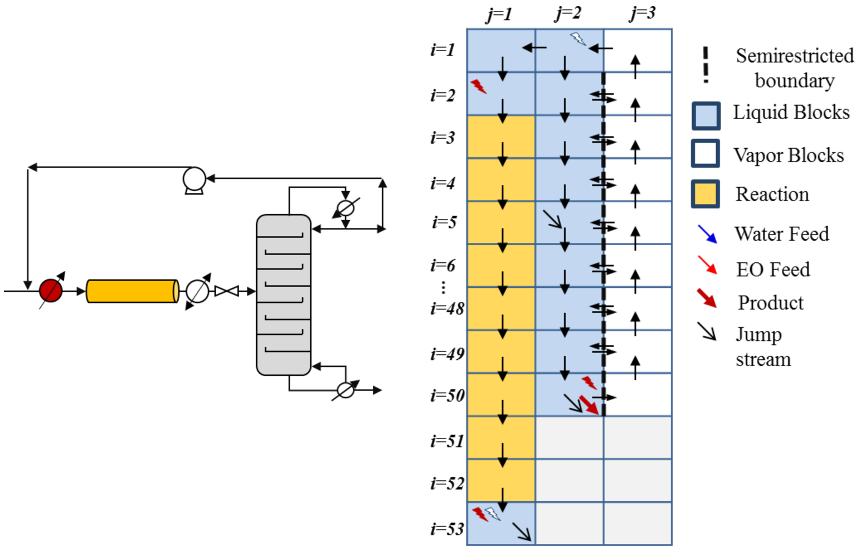
- Capital Investment
- Raw material Cost
- Hot and Cold Utility Costs

Minimize Total CO_2 emissions:

- Emissions pertained to EO Production
- Electricity
- Steam production

Representation of Base Case Designs

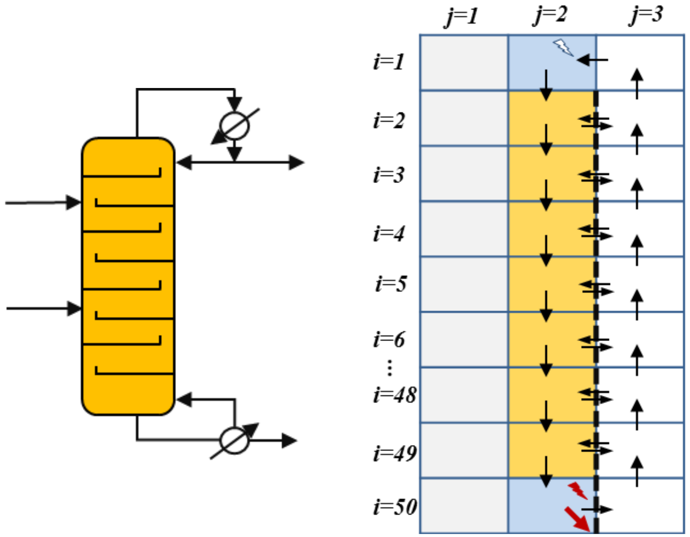
Not intensified: PFR-distillation-recycle



53 × 3 Superstructure:

Plug Flow Reactor (PFR): 50 building blocks (CSTRs-in-series)

Intensified: Single reactive distillation column

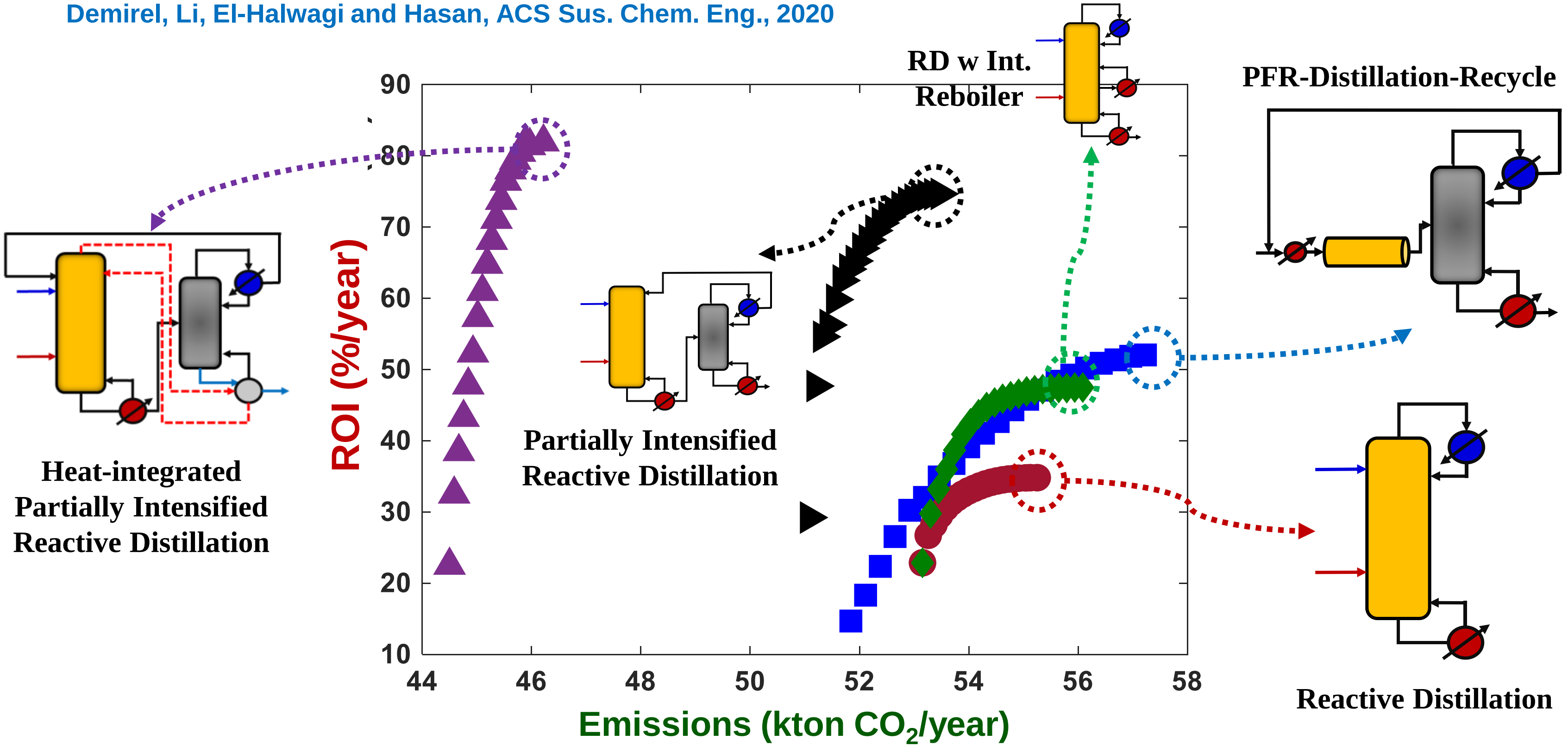


50 × 3 Superstructure:

50 Reactive/non-reactive V-L equilibrium block

Multiobjective Optimization

Demirel, Li, El-Halwagi and Hasan, ACS Sus. Chem. Eng., 2020



Ethylene Glycol (EG) Production

Demirel, Li and Hasan, Ind. Eng. Chem. Res., 2019

Minimize Total Annual Cost for 25 kmol/h EG production with 99.8% purity

Feeds:

- Ethylene Oxide (Sat'd Liquid at 1 atm)
- Water (Liquid at 298 K)

Reactions:

$$C_2H_4O + H_2O \rightarrow C_2H_6O_2$$

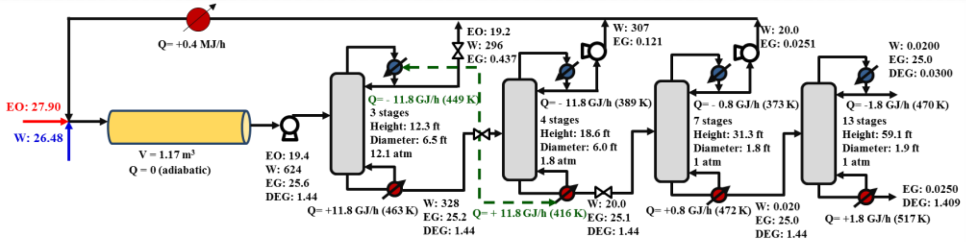
EthyleneOxide + Water → Ethylene Glycol

$$C_2H_4O + C_2H_6O_2 \rightarrow C_4H_{10}O_3$$

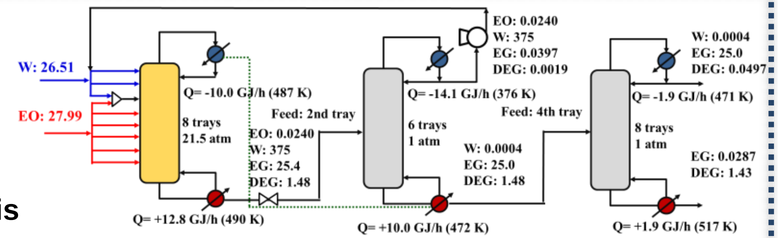
Ethylene Glycol + Etyhlene Oxide → Diethylene Glycol

- Liquid phase Homogeneous Reaction

Base-Case: Unit Operation-based Synthesis



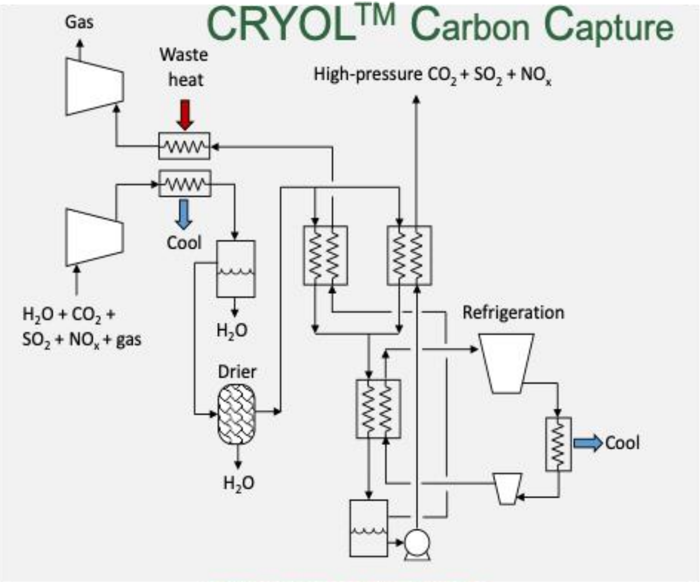
Building block-based Synthesis



3 major equipment instead of 5 (and 6% less cost)

Post-combustion CO_2 Capture

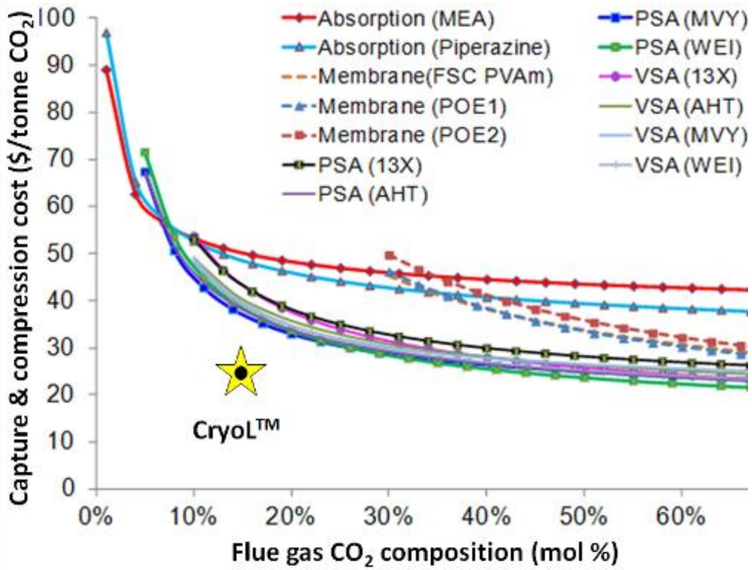
Most cost-effective cryogenic separation process for carbon capture



SIMPLIFIED SCHEMATIC

KEY FEATURES

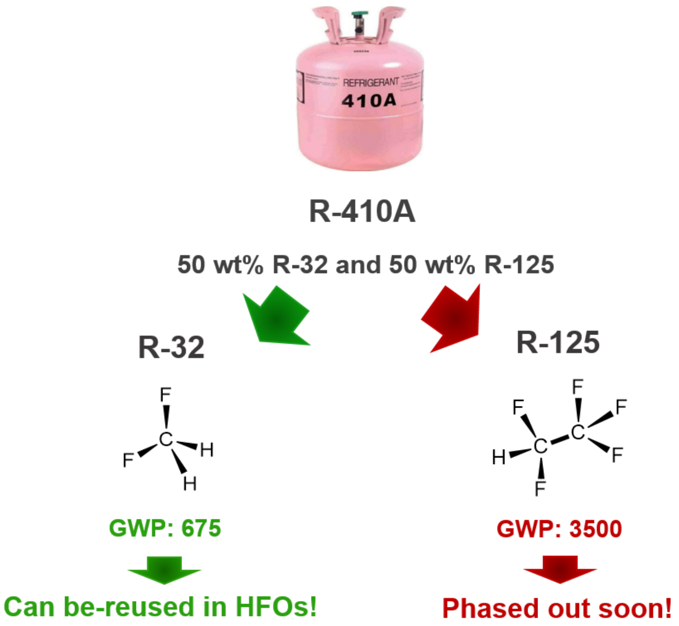
- Separates >90% CO_2, >99.99% SO_2, and >99.999% NO_x from coal-fired power plant flue gas
- No sorbents, adsorbents, membranes, or other expensive materials
- Flexible operation
- Less than \$25 per tonne CO_2 captured
- Extensive energy integration and utilization of waste heat
- Provisional patent filed



Co-inventors: Sadaf Monjur, Faruque Hasan, Mark Holtzapple

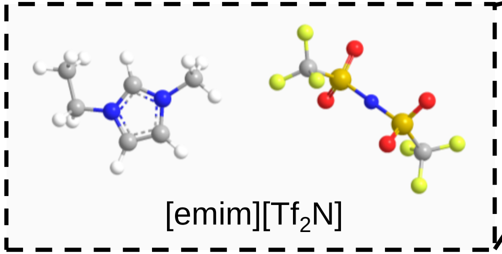
Separation of High-GWP Refrigerant Mixtures

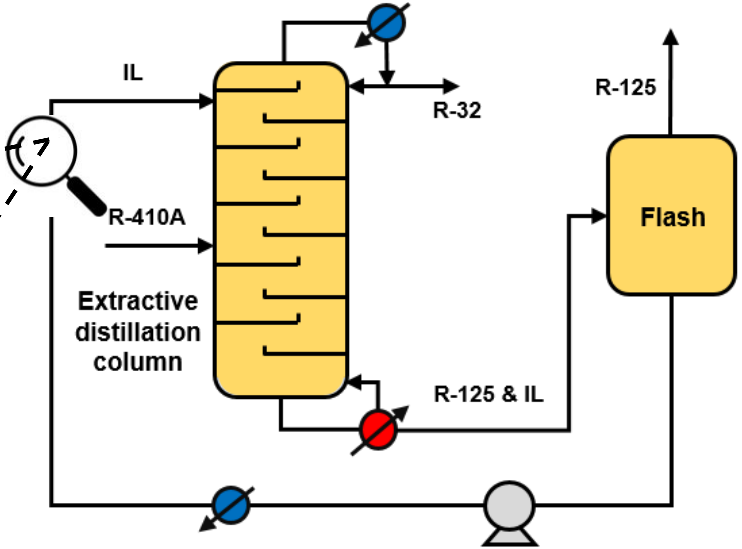
- More than 3 million tons of refrigerant are in use worldwide
- Hydrofluorocarbons (HFCs)
  - Some have global warming potential (GWP) up to 12,400 CO_2-eq. (Asensio-Delgado et al., 2021)
  - Leakage of refrigerants contributes to 7.8% of global GHG emissions (Harders et al., 2022)
- Market value of R-410A separation is over $1 billion
- Challenges in R-410a separation
  - Constituent refrigerants (R-32 and R-125) form azeotropic mixture
  - Conventional distillation-based separation becomes highly energy- and cost-intensive
  - Currently there exist no commercial separation techniques for refrigerant mixtures separation



Extractive Distillation-based Separation

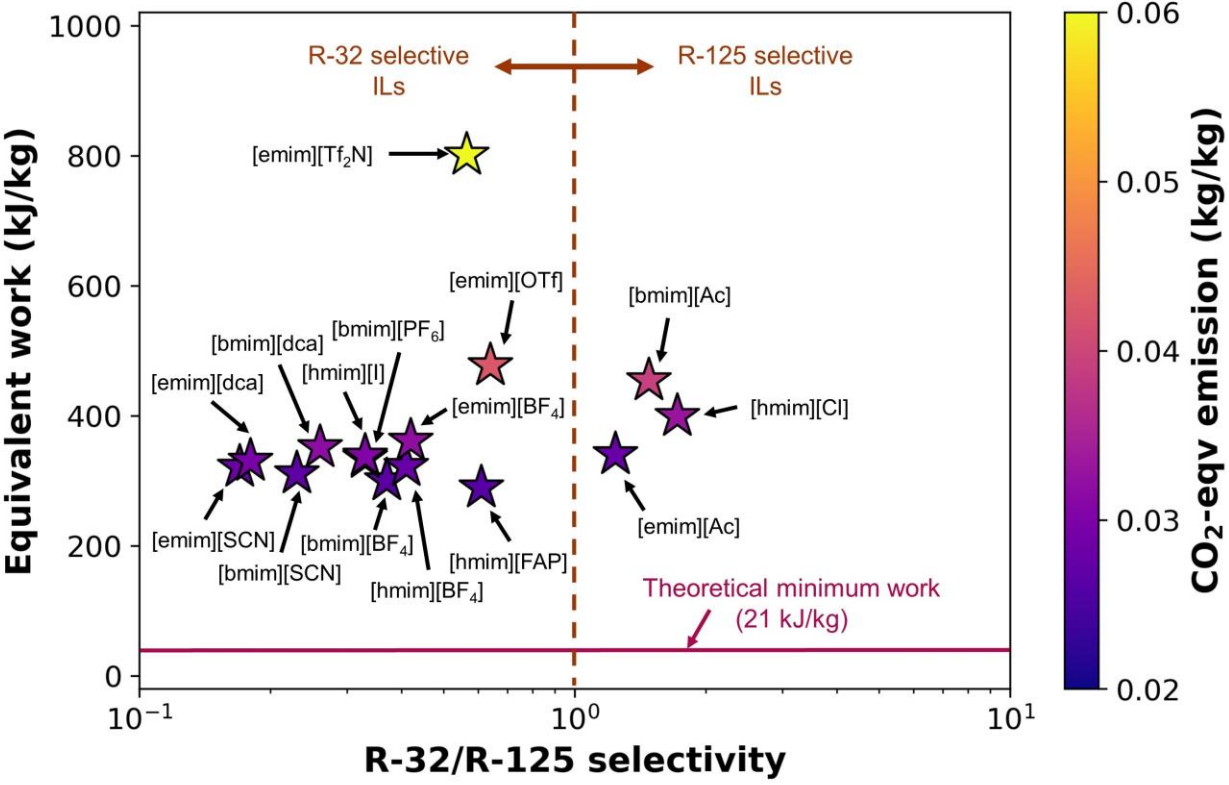
Extractive Distillation (ED) is an intensification technique that utilizes a high boiling point solvent to change the component relative volatilities





PROJECT EARTH

Process-based Screening of Existing Ionic Liquids



Concluding Remarks

- Process intensification shows potential for addressing some of the new and old challenges in the chemical process industry
- Representation is critical in systematic innovation in process intensification
- Design building blocks
  - Provide a seamless transition between phenomena, tasks, equipment and flowsheets
  - Allow optimization-based approach for automated flowsheet generation, process synthesis and intensification
  - Provide an initial starting point for approaching the central tradeoff in superstructure-based synthesis (between generality and tractability)
- Several outstanding challenges remain to be addressed
  - Generality: It is an open question how many rows and columns should be postulated in the initial superstructure
  - Tractability: New solution techniques are required considering inherent symmetry and degeneracy

Acknowledgement

Jianping Li
Keegstra Postdoctoral Researcher, University of Wisconsin–Madison

Salih Emre Demirel
Senior Research Specialist, Core R&D
Dow Chemical

Sadaf Monjur
PhD Student, Texas A&M University

National Science Foundation (NSF)

AIChE/RAPID Institute for Process Intensification

Department of Energy (DOE)

ACS Petroleum Research Fund

Professor Efstratios N. Pistikopoulos, TAMU
Professor Mahmoud El-Halwagi, TAMU
Professor Rafiqul Gani, PSE for SPEED

Sustainable Process Synthesis and Intensification for Industrial Decarbonization

Faruque Hasan, PhD

Artie McFerrin Department of Chemical Engineering, Texas A&M University
College Station, TX, USA

ARTIE MCFERRIN DEPARTMENT OF CHEMICAL ENGINEERING TEXAS A&M UNIVERSITY

TEXAS A&M UNIVERSITY Texas A&M Energy Institute

TEES Texas A&M Engineering Experiment Station

2022 Seminar for Energy Systems Initiative (ESI) at the Center for Advanced Process Decision-Making (CAPD)
November 09, 2022