Integrated Technology for Cost-Effective CO_2 Capture and Formic Acid Production: Modeling, Optimization and Economic Analysis

Maojian Wang[a,b], Jinliang Ma[a,b], Brandon Paul[a,b], Miguel Zamarripa[a,b], Anthony Burgard[a]

a) National Energy Technology Laboratory, 626 Wallace Rd, Pittsburgh, PA,15236

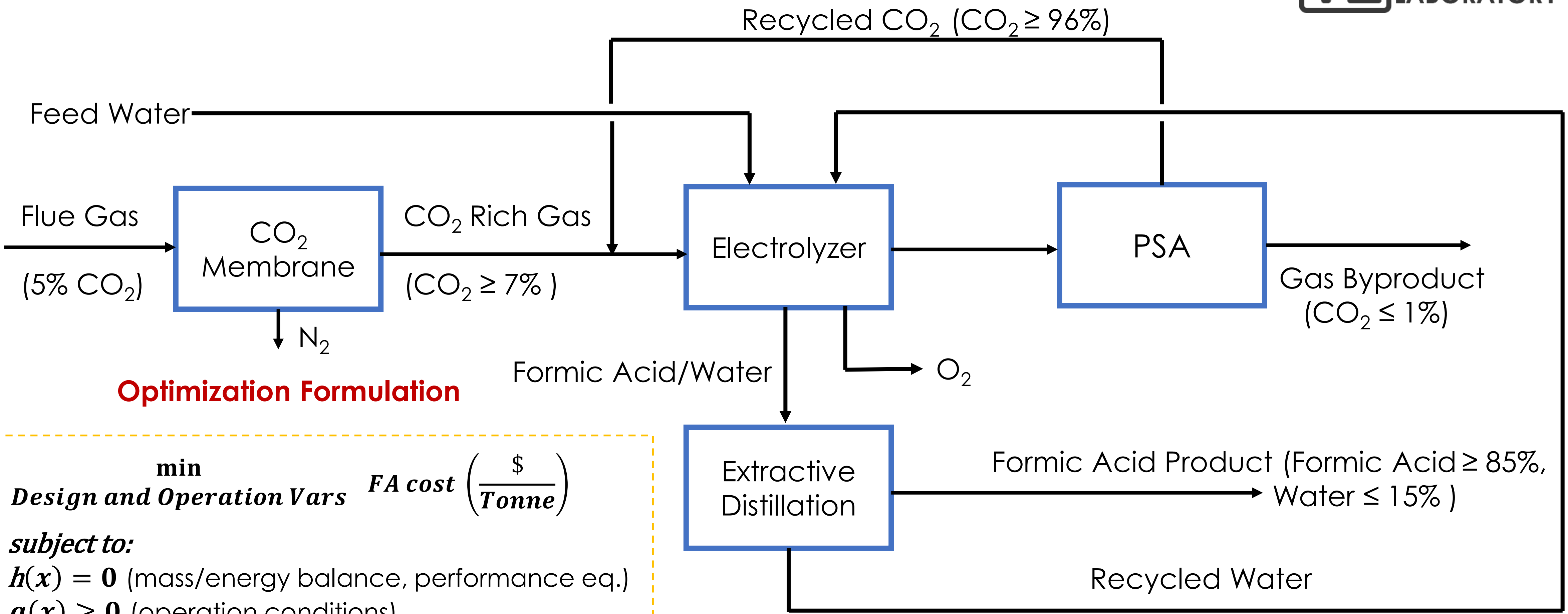
b) NETL support contractor, 626 Wallace Rd, Pittsburgh, PA,15236

Background and Motivation

- The high costs of traditional Carbon Capture and Storage (CCS) technologies highlight the need for more cost effective solutions to reduce CO_2 emissions.
- CO_2 Utilization potentially reducing costs by up to $45 per ton [1]
- The National Energy Technology Laboratory (NETL) is exploring efficient carbon utilization methods, focusing on electrochemical conversion of CO_2 into valuable chemicals.
- This work focuses on identifying the optimal design and operation of an integrated membrane-based CO_2 capture unit with the electrochemical conversion process to produce formic acid.

[1] Smith E, Morris J, Kheshgi H, Teletzke G, Herzog H, Paltsev S. The cost of CO2 transport and storage in global integrated assessment modeling. International Journal of Greenhouse Gas Control. 2021 Jul 1;109:103367.

Reactive Capture Technology Process and Optimization



Optimization Formulation

$$\min_{\boldsymbol{Design\ and\ Operation\ Vars}} \boldsymbol{FA\ cost}\left(\frac{\$}{\boldsymbol{Tonne}}\right)$$

subject to:

$\boldsymbol{h(x) = 0}$ (mass/energy balance, performance eq.)

$\boldsymbol{g(x) \geq 0}$ (operation conditions)

$$\boldsymbol{FA\ cost} = \frac{\boldsymbol{Annualized\ CAPEX + Fixed\ O\&M + Variable\ O\&M}}{\boldsymbol{Formic\ Acid\ production}}$$

$CO_2 + H_2O \rightarrow HCOOH + ½\ O_2$

IDAES: Equation-Oriented Open-Source PSE Package[2]

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2020 R&D 100

IDAES Core

Modeling Framework

Hierarchical - Steady-State & Dynamic - Model Libraries

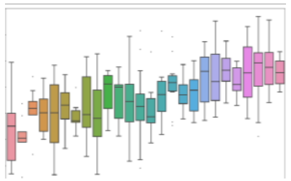
Advanced Equation Oriented Solvers

PYOMO

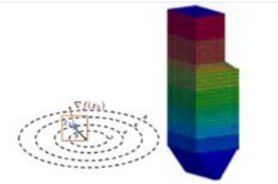
Flexible Programming Foundation

python

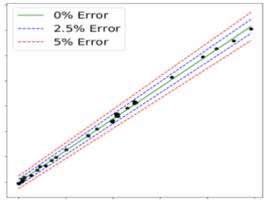
IDAES UQ and AI



Data Reconciliation



Multi-Scale Modeling and Optimization



Parameter Estimation

PySMO

PyROS

Optimization & Uncertainty Quantification

IDAES

Institute for the Design of Advanced Energy Systems

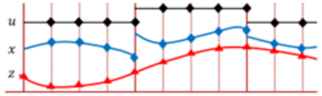
IDAES Enterprise

Electricity Grid Modeling

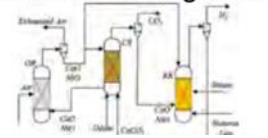
Expansion planning

IDAES Operation and Design

Process Dynamics



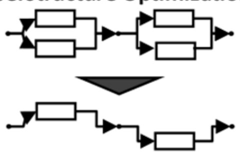
Process Design, Optimization & Integration



Process Control

caprese

Conceptual Design via Superstructure Optimization



PYOMO DAE

Trajectory optimization, optimal control, state/parameter estimation

[2] Lee, Andrew, Jaffer H. Ghouse, John C. Eslick, Carl D. Laird, John D. Siirola, Miguel A. Zamarripa, Dan Gunter et al. "The IDAES process modeling framework and model library—Flexibility for process simulation and optimization." Journal of Advanced Manufacturing and Processing 3, no. 3 (2021): e10095. https://doi.org/10.1002/amp2.10095

1-Dimensional High CO_2 Selective Membrane Model

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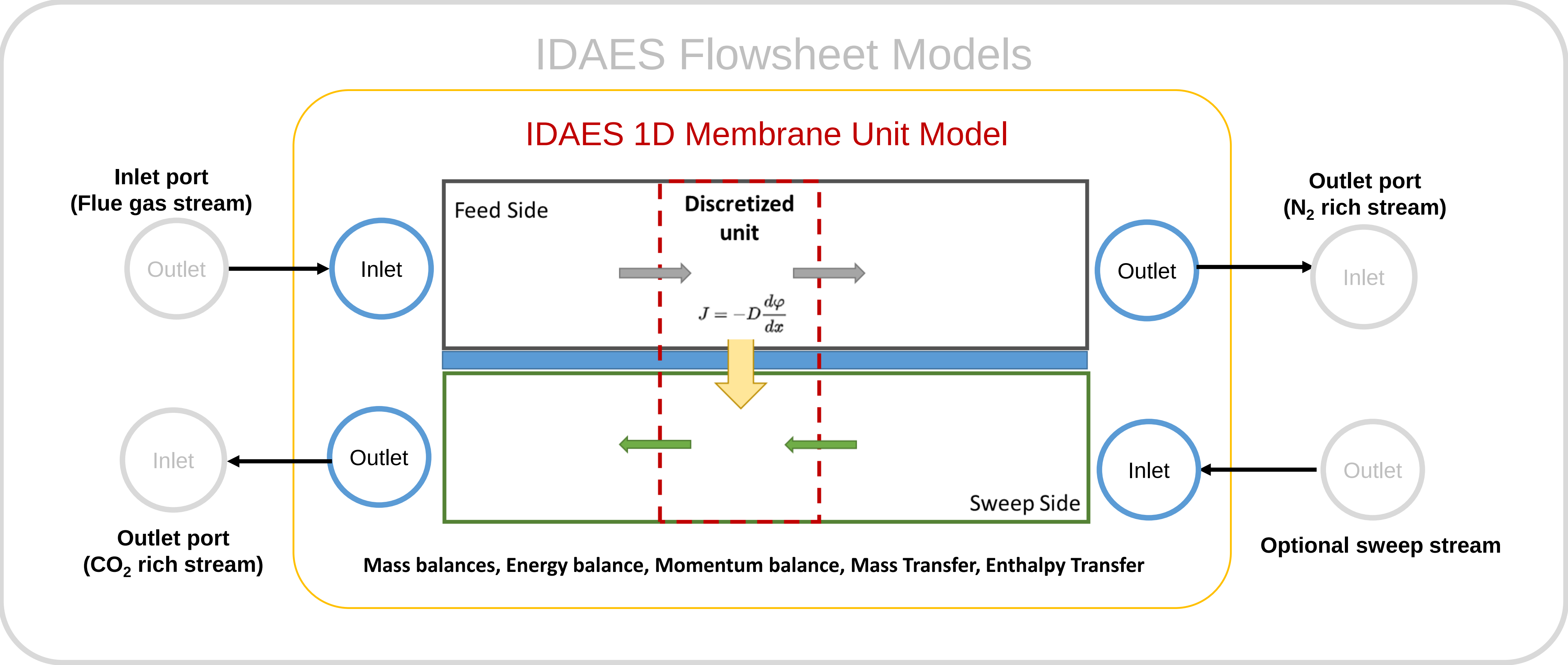
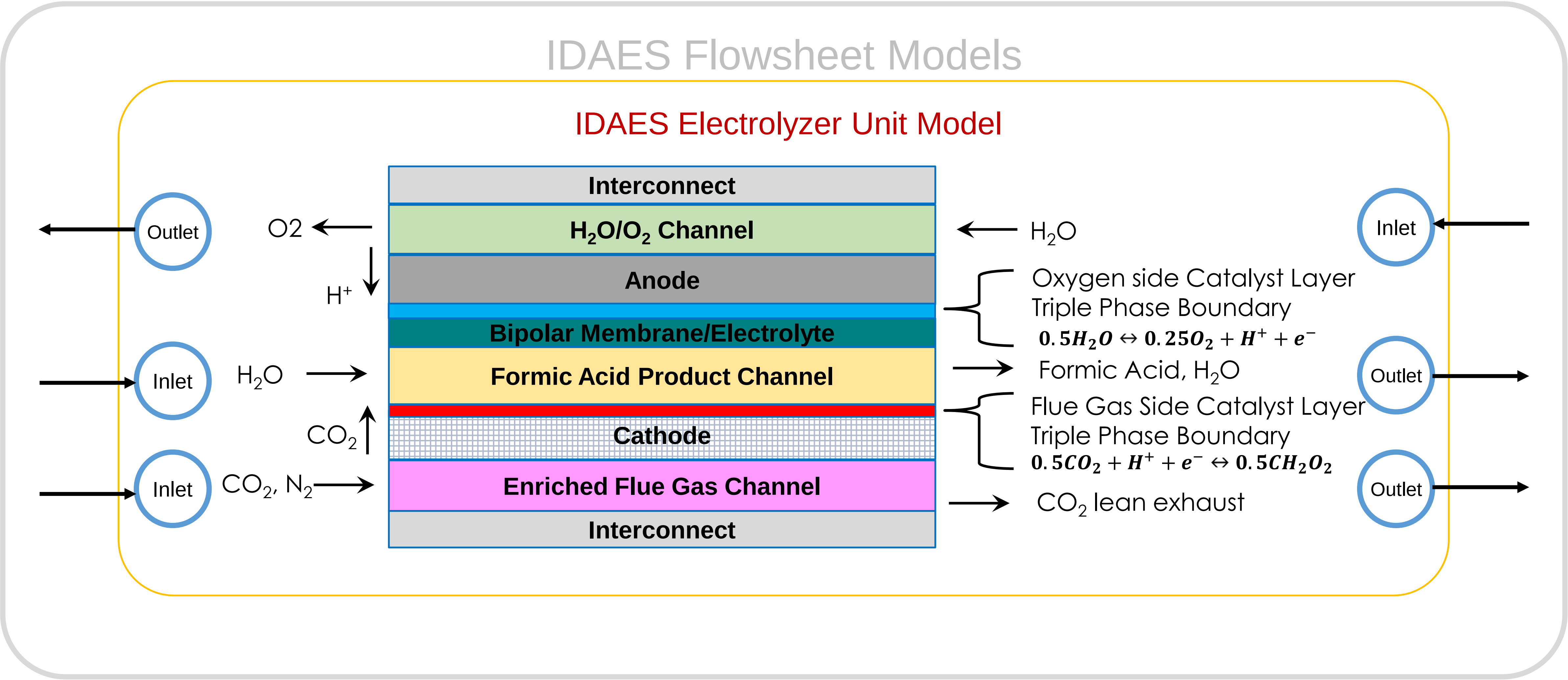
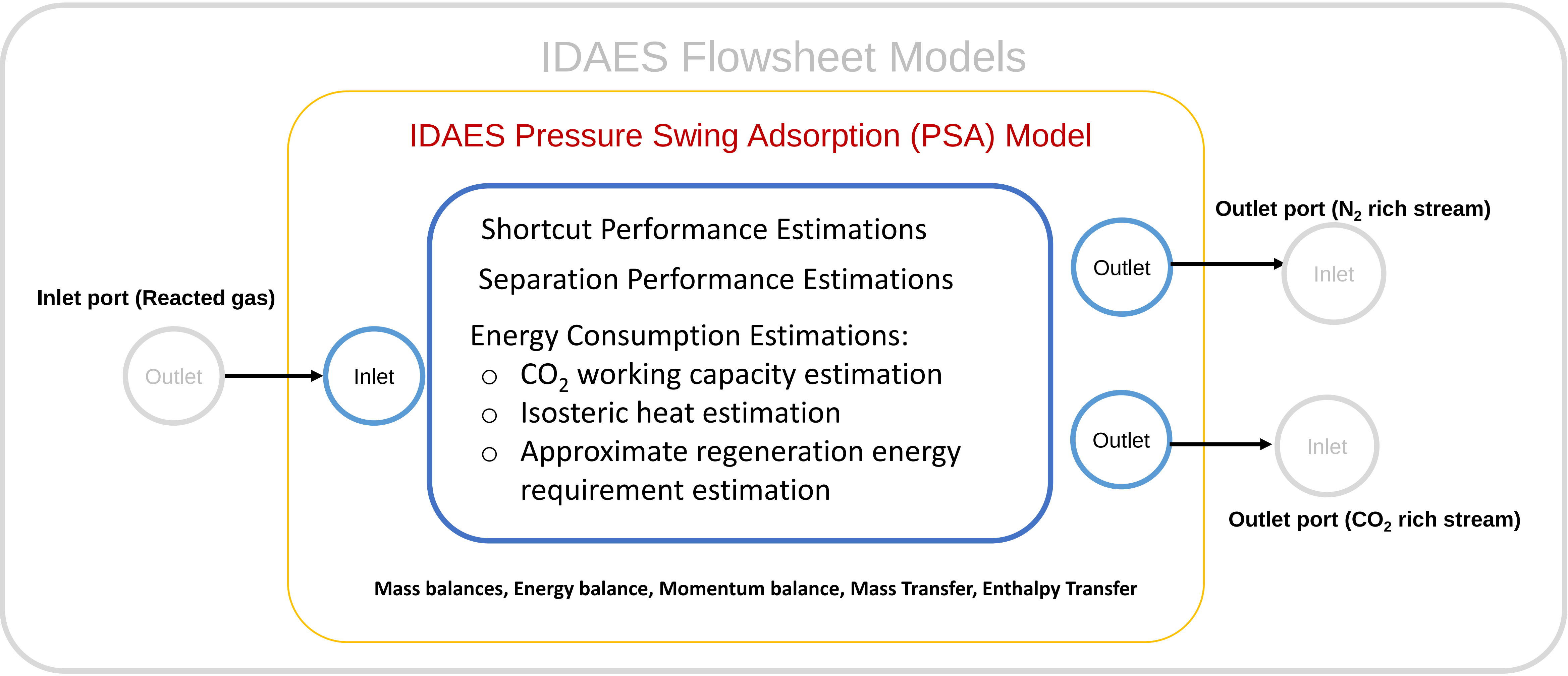


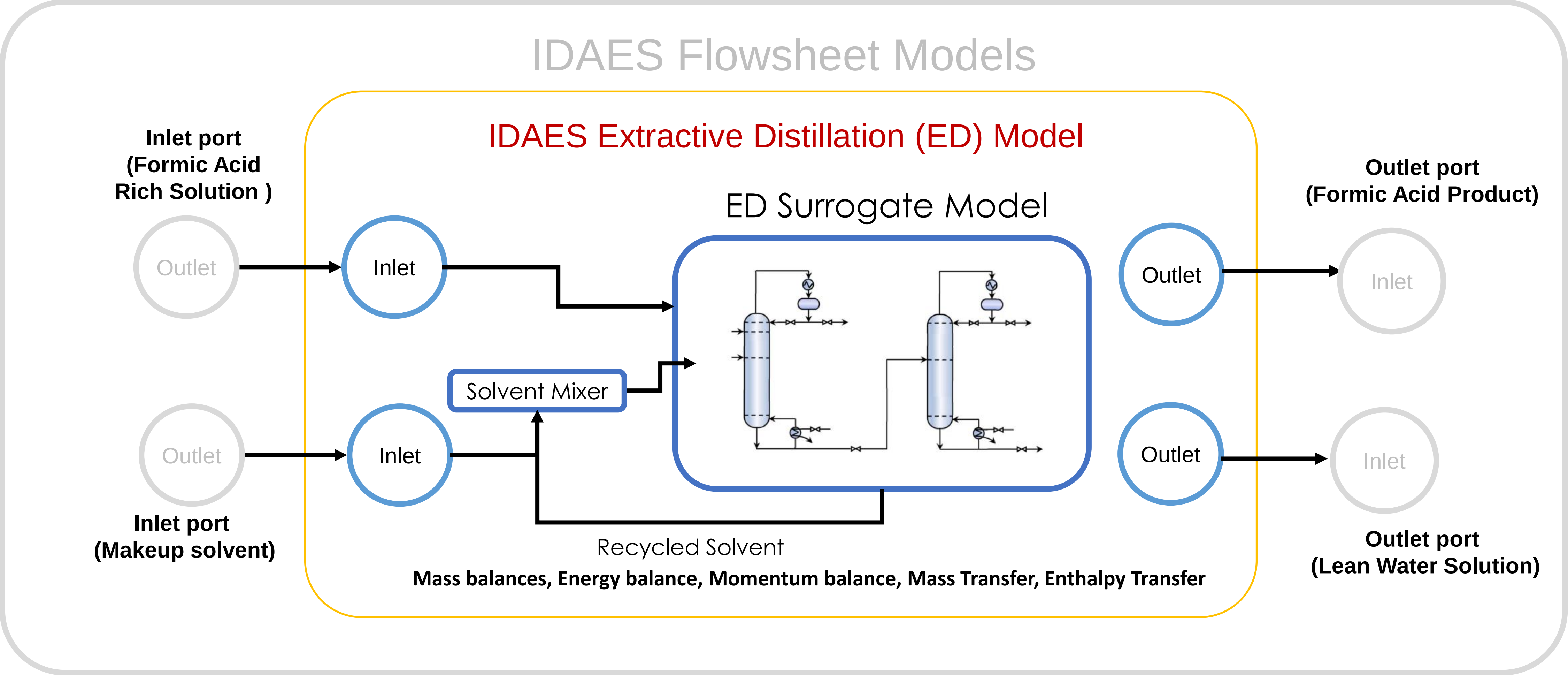
1-D Electrolyzer Cell Model for Formic Acid Production



Pressure Swing Adsorption (PSA) Shortcut Model



Extractive Distillation (ED) Model



Extractive Distillation Surrogate Model

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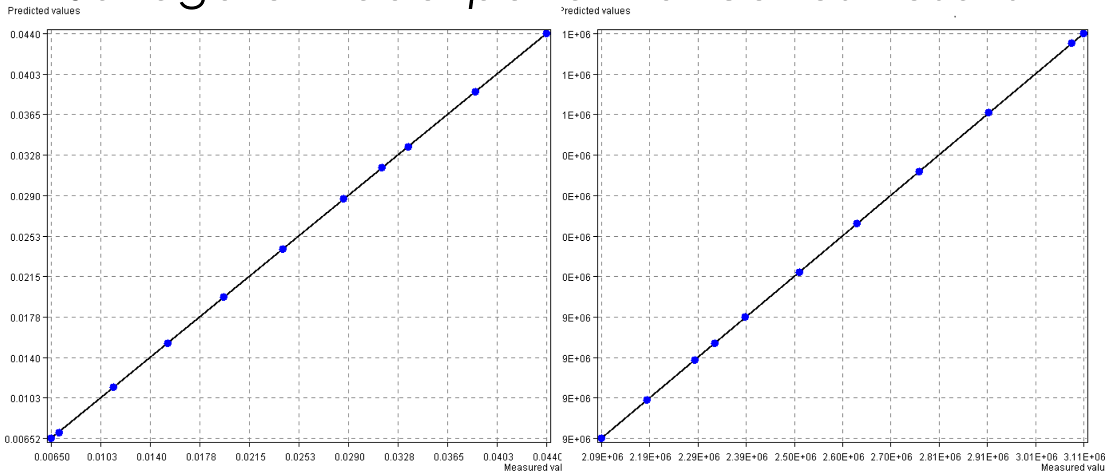
- Aspen Simulation Assumptions [3] :
  - Total tray numbers of distillation column
    - Extractive Distillation Column: 23
    - Entrainer Recovery Column: 8
  - Feed positions in distillation column
    - Extractive Distillation Column: 3 (SULFO), 11(FA)
    - Entrainer Recovery Column : 3
  - Solvent type: SULFO $100_{wt}\%$

Surrogate model performance test results



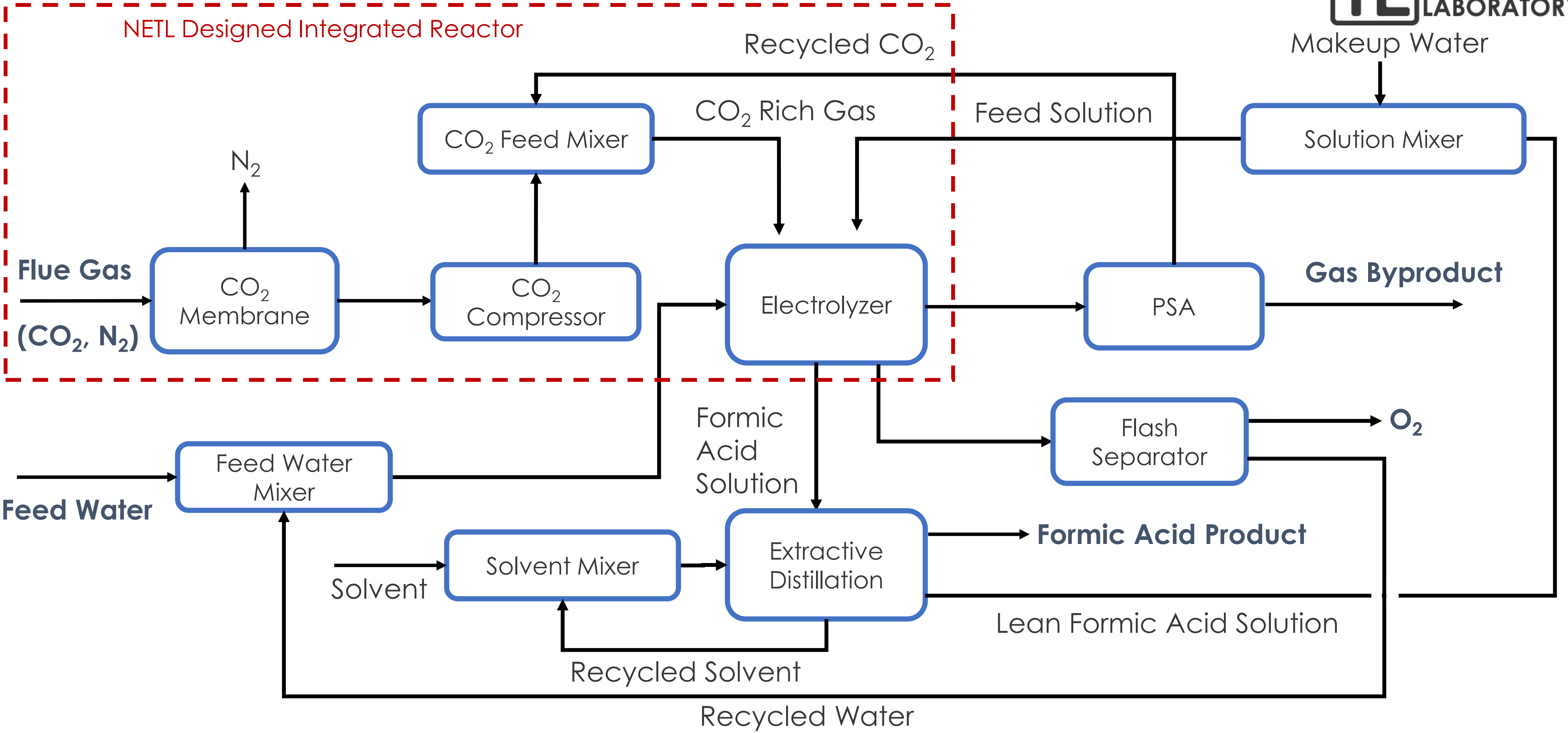
Formic acid production *Reboiler Duty*

- Surrogate Modelling:
  - ➢ Input variables: Formic acid solution feed composition (3.5 %~20 mol%)
  - ➢ Machine Learning method : ALAMO (Automatic Learning of Algebraic MOdels)[4]
  - ➢ Outputs: Recovery fractions, reboiler, condenser and colling duties per kg of feed processed

U.S. Department of ENERGY

[3] Ge, Xiaolong, et al. "Optimization and control of extractive distillation for formic acid-water separation with maximum-boiling azeotrope." Computers & Chemical Engineering 169 (2023): 108075.
[4] https://minlp.com/alamo

IDAES Flowsheet Model for NETL Reactive Capture Tech



CO_2 to Formic Acid Conversion - Case Study Summary

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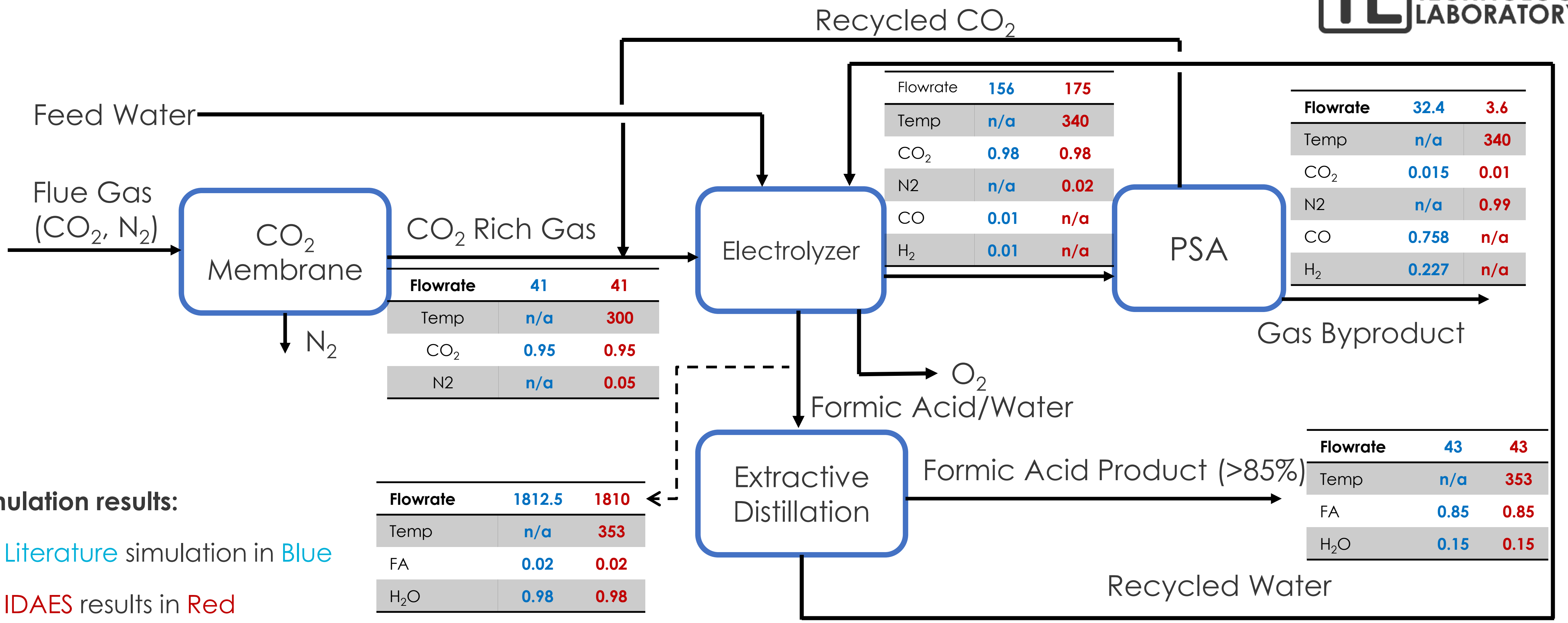
Items	Literature Base Case[5]	NETL Experimental Case
Reference	Aspen Plus	-
Membrane Materials	Literature Reference	NETL Lab-Scale Prototype
Electrolyzer	Fixed Conversion	1-D model
Membrane	Fixed Separation	1-D model
Production Rate (85% purity)	6450 kg/hr (43 mol/s)	6450 kg/hr (43 mol/s)
CO_2-rich Gas Inlet to Electrolyzer	High CO_2 Purity (≥ 95%)	Medium/Low CO_2 Purity (7% ~ 20 %)

[5] Shannon M. et al., Screening Techno-Economic Analysis of NETL Reactive Capture Technology, 09/30/2022

Verification Results



CO_2 Rich Gas:

Flowrate	41	41
Temp	n/a	300
CO_2	0.95	0.95
N2	n/a	0.05

Electrolyzer to PSA:

Flowrate	156	175
Temp	n/a	340
CO_2	0.98	0.98
N2	n/a	0.02
CO	0.01	n/a
H_2	0.01	n/a

Gas Byproduct:

Flowrate	32.4	3.6
Temp	n/a	340
CO_2	0.015	0.01
N2	n/a	0.99
CO	0.758	n/a
H_2	0.227	n/a

Formic Acid Product:

Flowrate	43	43
Temp	n/a	353
FA	0.85	0.85
H_2O	0.15	0.15

Recycled Water:

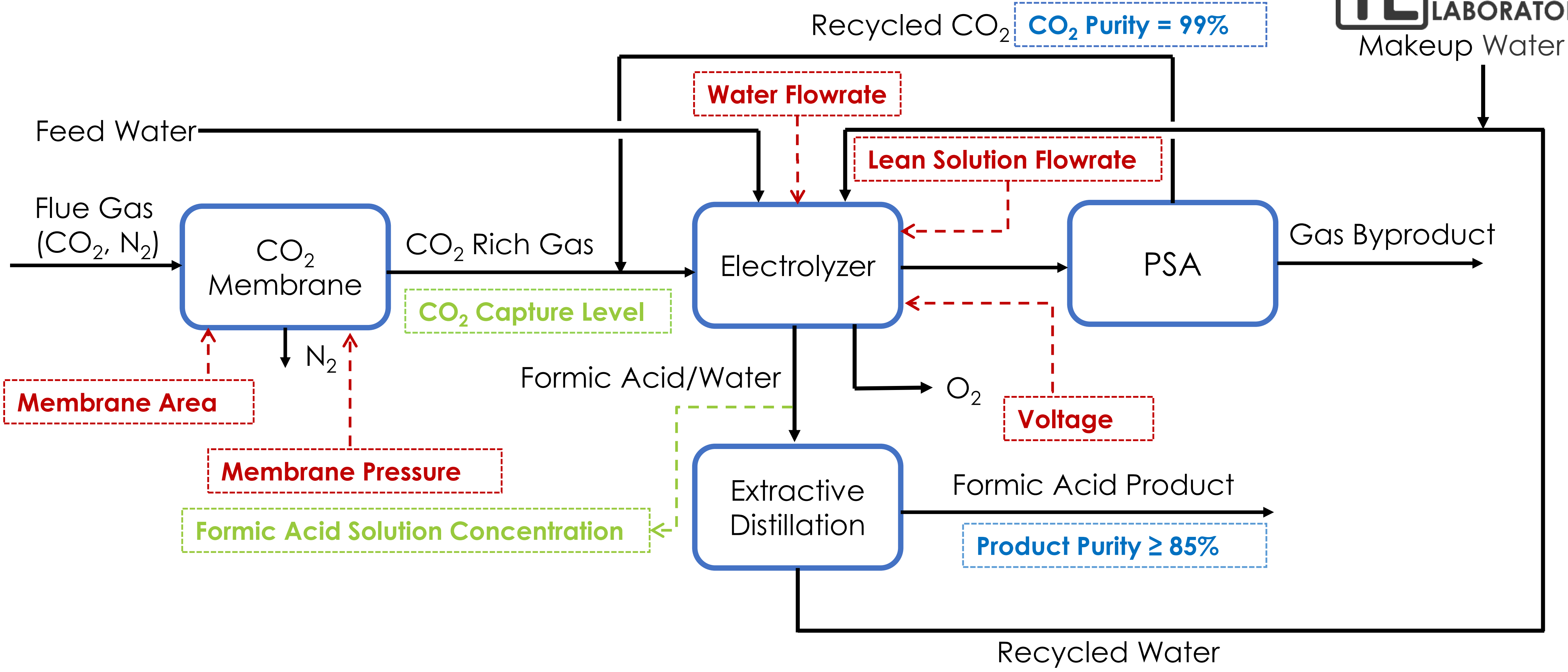
Flowrate	1812.5	1810
Temp	n/a	353
FA	0.02	0.02
H_2O	0.98	0.98

Simulation results:

- Literature simulation in Blue
- IDAES results in Red
- Flowrate unit in mol/s
- Temperature unit in K

IDAES EO Model:
- Accurate predictive models that match Aspen simulation results.
- Contributed first-principles open-source models and property packages.
- Rigorous models can be used to simultaneously optimize design and operating conditions.

Optimization Variables in NETL Reactive Capture Technology



Optimization Variables in red, Free Variables in green, Constraints in blue

Optimization Problem and Results

- Objective Function: $$\min \text{LCOP} = \frac{\text{Total Annualized Cost}}{\text{Total Annual Formic Acid Production}}$$
- Model Statistics:
  - Number of variables : 1465; Number of constraints : 1460
  - Solver : IPOPT; all problems solved under 35 iterations.

Variables	Unit	Lower Bound	Upper Bound	Initial Values	Optimal Values
Membrane Area	m^2	10000	30000	20000	14416
Membrane Pressure	bar	0.5	2	1	0.51
Electrolyzer Voltage	V	1	4	3	3.002
Water Flowrate	mol/s	300	600	420	363
Lean Solution Flowrate	mol/s	300	600	427	305

Optimization Results of NETL Reactive Capture Technology

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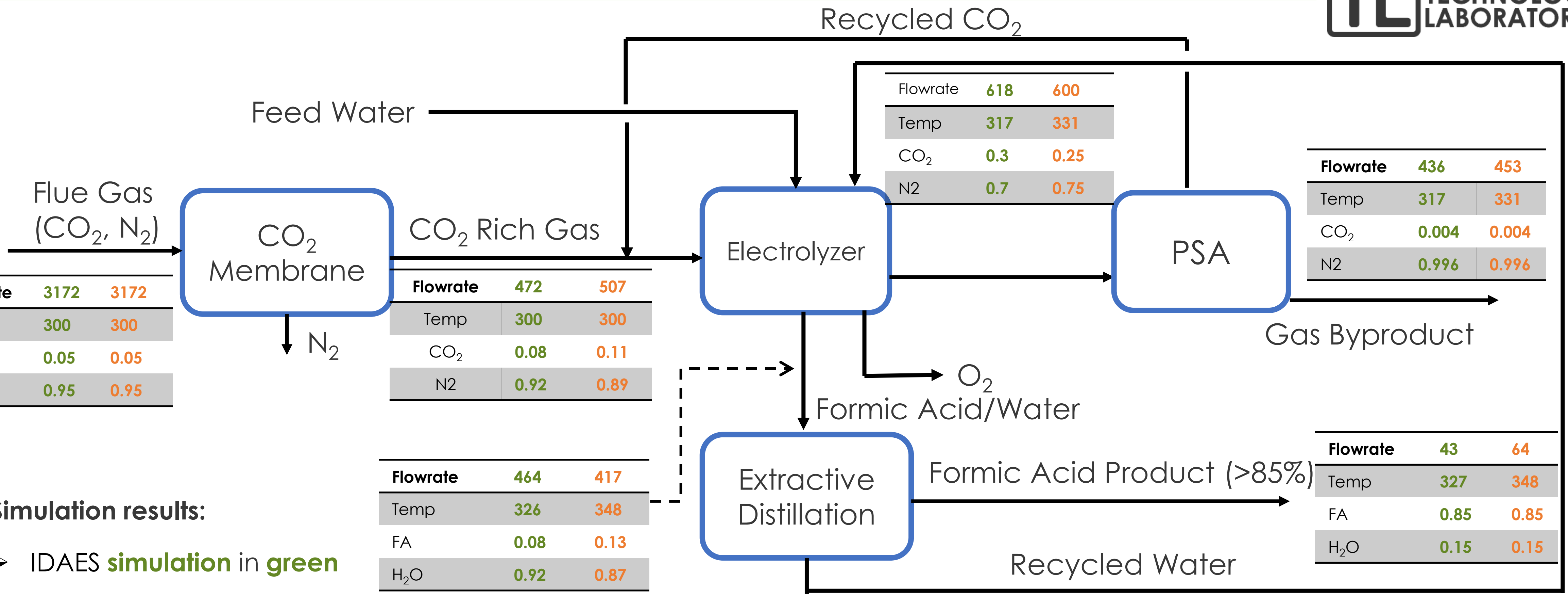


Flowrate	3172	3172
Temp	300	300
CO_2	0.05	0.05
N2	0.95	0.95

Flowrate	472	507
Temp	300	300
CO_2	0.08	0.11
N2	0.92	0.89

Flowrate	618	600
Temp	317	331
CO_2	0.3	0.25
N2	0.7	0.75

Flowrate	436	453
Temp	317	331
CO_2	0.004	0.004
N2	0.996	0.996

Flowrate	464	417
Temp	326	348
FA	0.08	0.13
H_2O	0.92	0.87

Flowrate	43	64
Temp	327	348
FA	0.85	0.85
H_2O	0.15	0.15

Simulation results:

- IDAES **simulation** in **green**
- IDAES **optimization** in **orange**
- Flowrate unit in mol/s
- Temperature unit in K

- The membrane limiting factor is CO_2 permeability.
- The electrolyzer's optimal performance is reached when the voltage is 3.002 V.
- The maximum production of formic acid is obtained given the electrolyzer's size.
- The tradeoff between maximizing production and minimizing cost involves electrolyzer efficiency, membrane size, and extractive distillation duties.

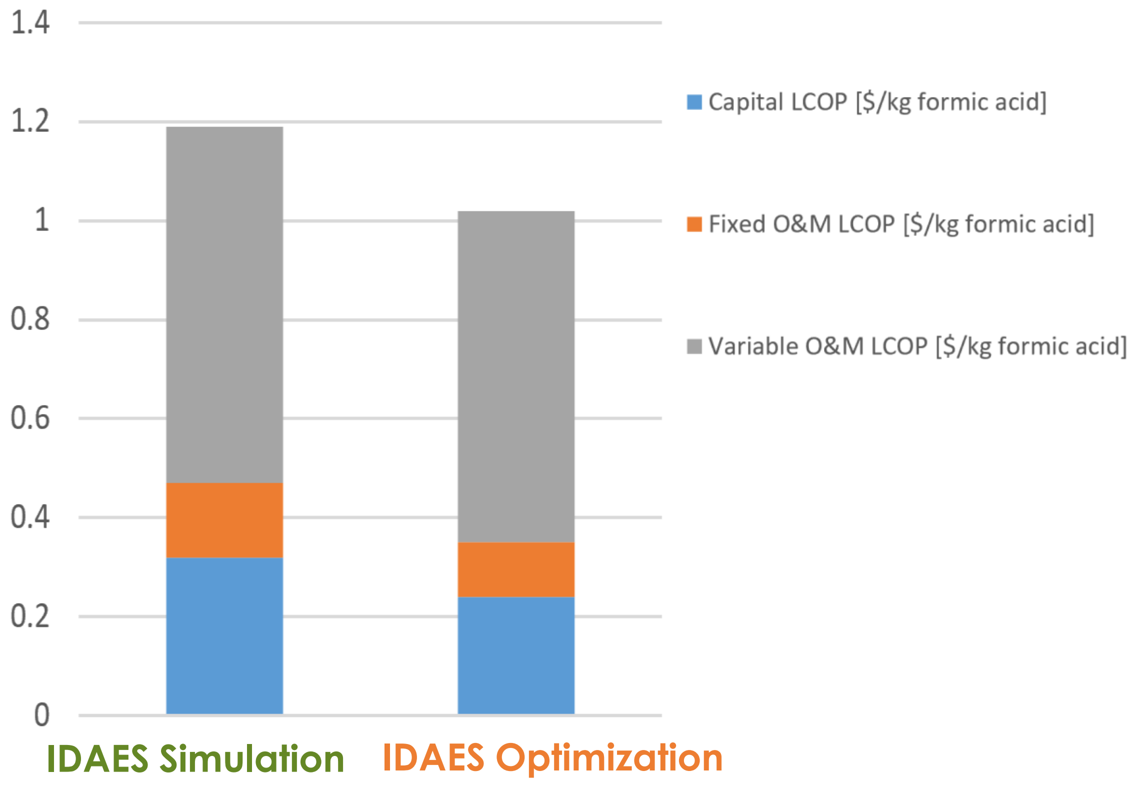
Economic Analysis Results

- Performance Index: Levelized Cost of Production (LCOP)

$$LCOP = \frac{\text{Total Annualized Cost}}{\text{Total Annual Formic Acid Production}}$$

Assumptions	Values
Electricity price	$71.7 /MWh
Water price	$1.9 / 1000 gals
Flue gas cost	$0
Capacity	85 %
Plant lifetime	31 years
FCR	6.64 %
TASC factor	1.047
CCF	6.96 %

LCOP Comparisons



LCOP decreased ~ 14% after optimization (from 1.19 to 1.02 $/kg formic acid)

Conclusions

- IDAES PSE modelling framework enabled process design and off-design performance optimization for NETL's reactive capture system.
- Sensitivity analysis showed trade-off between LCOP, design variables and limiting factors.
- This work identified optimal operating conditions and process design, results can be leveraged by NETL's experimental team to analyse different process configurations and/or operating scenarios.

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https://idaes.org/about/contact-us/

2024 Joint IDAES/CCSI$_2$/PrOMMiS Technical Team Meeting
Lawrence Berkeley National Lab

Thanks!

Q & A