NATIONAL ENERGY TECHNOLOGY LABORATORY

Physics-based Modeling for Advancing Carbon Capture Technology Development

Madhava Syamlal

Focus Area Leader, Computational and Basic Sciences

Anthony V. Cugini

Director, Office of Research & Development

Carbon Capture 2020, U. of Maryland, October 5-6, 2009.

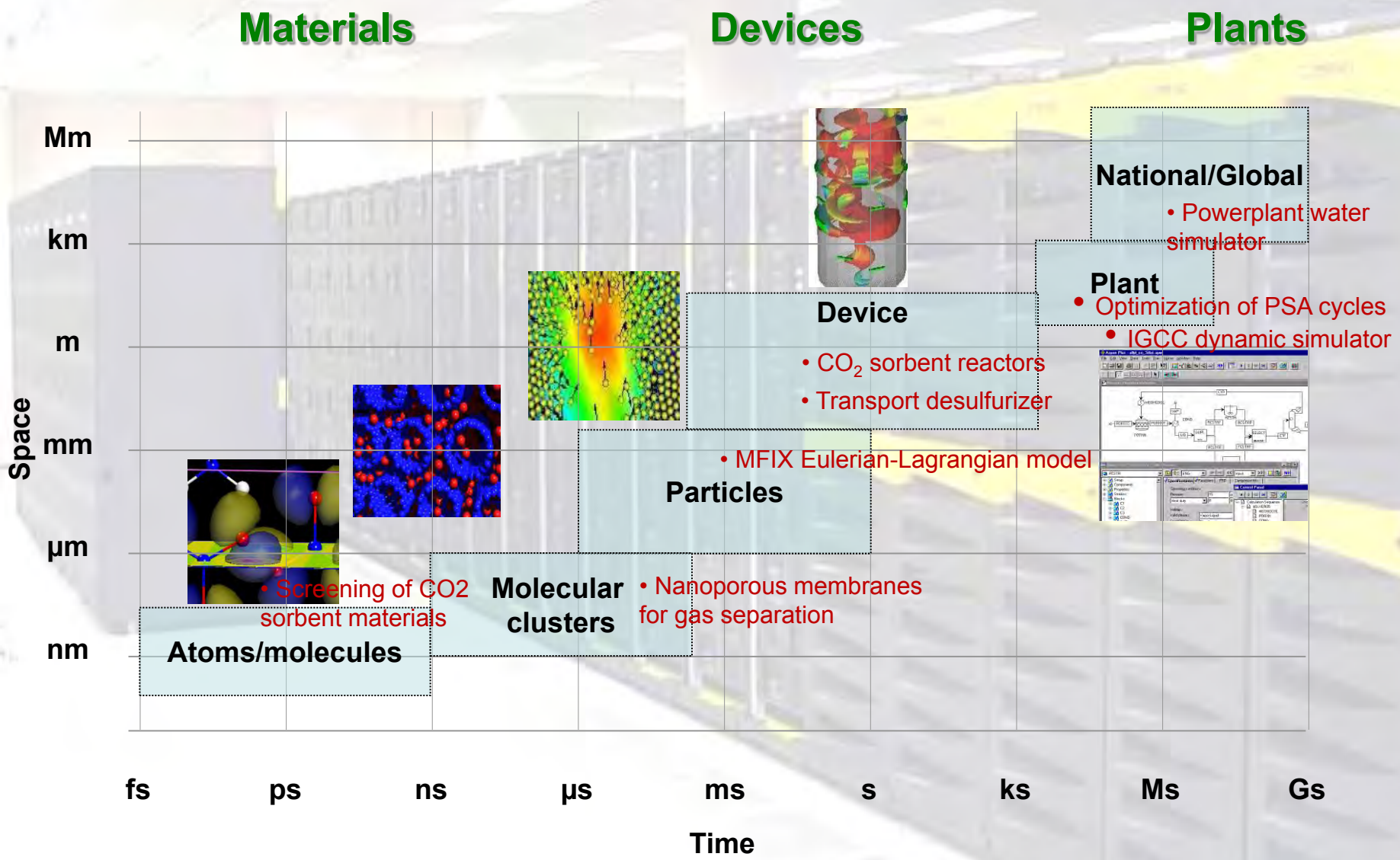
Motivation – 1

- **The lag time between discovery and commercial deployment of technologies for energy conversion is of the order of 2-3 decades**
- **Although commercial technologies are available, post-combustion capture poses several challenges**
  - Factor of 5 increased CO_2 capture capability
  - Significantly reduced cost of capture
  - Accelerated deployment
- **Need new approaches to take concepts from lab to power plant, quickly at low cost**

Motivation – 2

- **Here we discuss the use of physics-based modeling for accelerating technology development**
  - Computational screening to enable rapid identification of better materials (sorbents, membranes, catalysts)
  - Improving designs to achieve optimal device- and plant-scale performance
  - Having designs perform correctly the first time at every scale, reducing or eliminating the cost and time for adjustments or modifications
  - Skipping costly intermediate-scale steps on the pathway to commercialization

Examples of Modeling at Various Scales



Computational Screening CO_2 Sorbents

Screening Methodology

- Pre-select
- ab initio energetic calculations
- Lattice phonon calculations to obtain chemical potential of the reaction.
- Surface reaction kinetics
- Particle-scale reaction kinetics
- Device- and process-scale modeling

Solids Bank → Filter 0

$|\Delta E^{DFT}|<|E_0|$ → Filter 1

Good Candidates

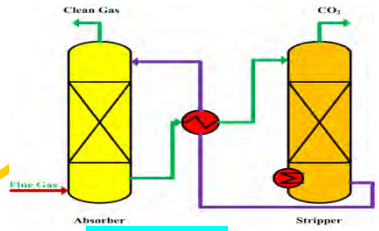
Min($|\Delta\mu|$) → Filter 2

$$\Delta\mu(T,P) = \Delta\mu^0(T) - RT(\ln P_{CO_2} \mp \ln P_{H_2O})$$

Thermodynamics

Better Candidates

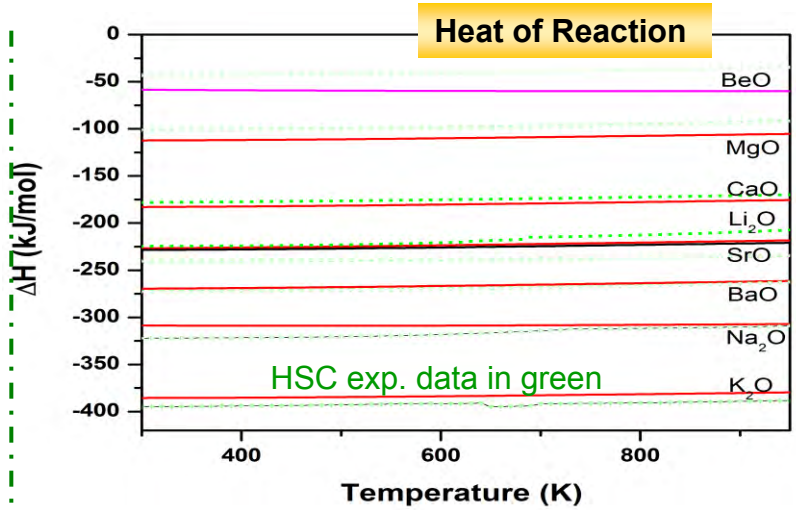
Fine Tune → Filter 3

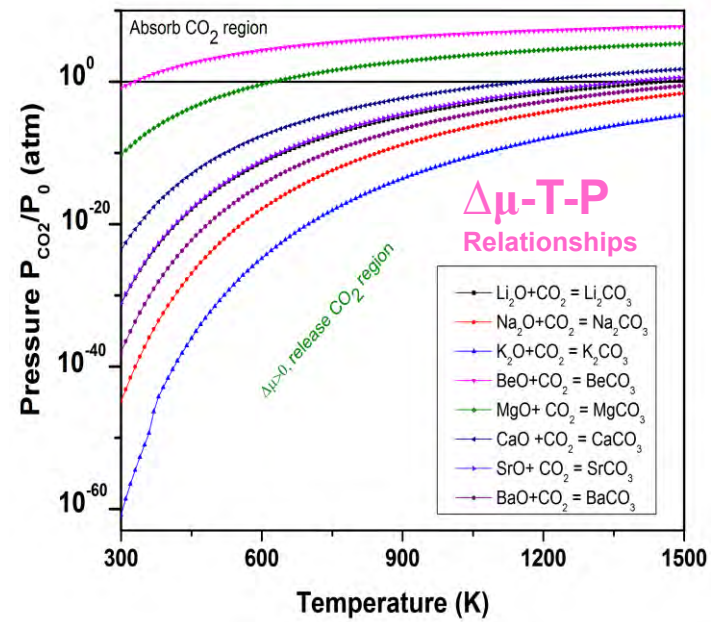


$$\frac{Q}{m_c} = \underbrace{\frac{m_e}{m_c}\cdot C_e\cdot\Delta T}_{\text{Heating the "equipment"}} + \underbrace{\frac{B}{L}\cdot C_s\cdot\Delta T}_{\text{Heating The sorbent}} + \underbrace{C_{p,c}\cdot T_2 - C_s\cdot T_1}_{\text{Enthalpy change between gaseous } CO_2 \text{ and sorbent}} + \underbrace{\frac{Q_r}{m_c}}_{\text{Heat of reaction}}$$

Best Candidates → Send for Experimental Evaluations

Very few good candidates left





Y. Duan and D. C. Sorescu, Phys. Rev. B 79 (2009) 014301

Design Ionic Liquids with Molecular Simulations

Ab initio QM

- Energy, structure
- Charge, force field
- Interaction mechanisms

Classical force-field

$$V_{tot} = \sum_{bonds} k_b (r - r_0)^2 + \sum_{angles} k_\theta (\theta - \theta_0)^2 + \sum_{dihedrals} k_\chi \left[1 + \cos(n\chi - \delta)\right] + \sum_{impropers} k_\psi (\psi - \psi_0)^2 + \sum_{i=1}^{N-1} \sum_{j>i}^{N} \left\{ 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right] + \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} \right\} + U_{pol}$$

Monte Carlo

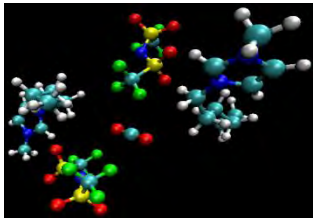
•Thermo dynamic Properties

Molecular Dynamics

•Transport Properties

- Henry's law constant
- Mixed gas selectivity
- Transport coefficients
- Permeability, permeability selectivity
- Heat of mixing, heat capacity
- Interaction mechanism: physical, chemical, Intermolecular complex

❖Search for better ILs
❖Modify IL functionality
❖Discover new IL



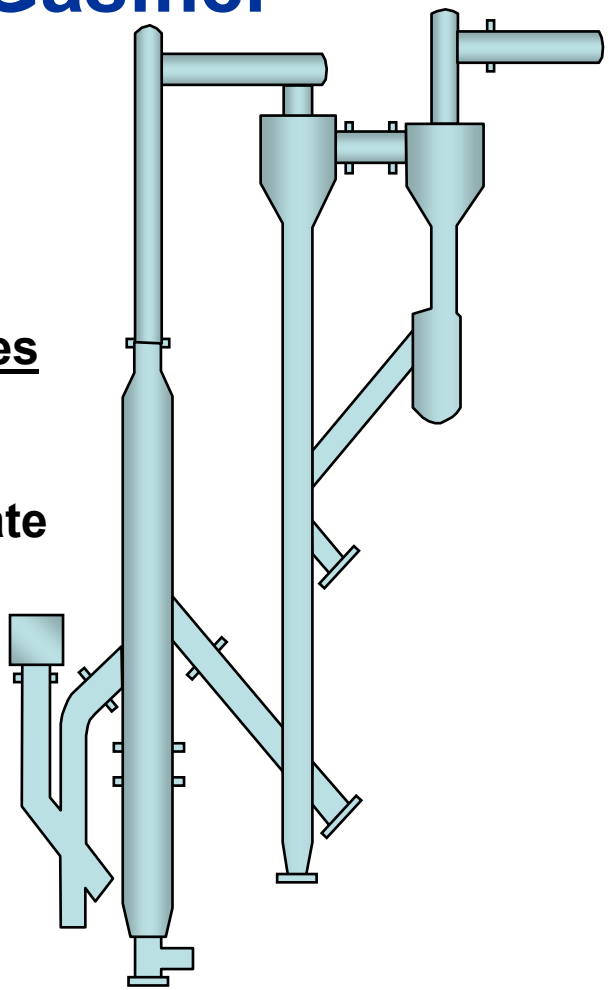
A new ionic liquid that exhibits *high CO_2 permeability* and *CO_2/H_2 selectivity was* identified with this method.

Changing Design Paradigm: Scaling-up a Transport Gasifier

13 MWth pilot-scale

Computational Studies

- **Length/Diameter**
- **Coal feed rate**
- **Solids circulation rate**
- **Recycled syngas**
- **Coal jet penetration**

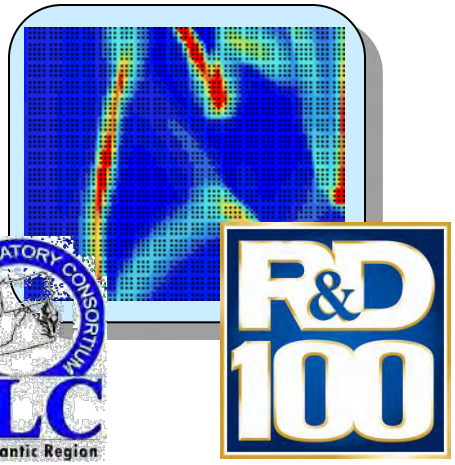


285 MWe Commercial-scale

	Pilot	*Comm.*
Coal Feed (kg/s)	*0.6*	*30*
Pressure (atm)	*17*	*32*
Power (MW)	*13 (th)*	*285 (e)*

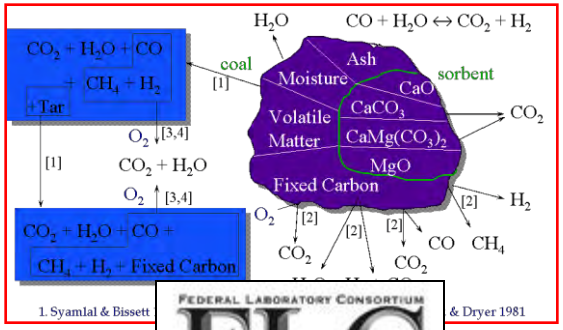
Gasifier Model: Leverages NETL Expertise in Multiphase Flow Modeling

- **Confluence of two areas of research pioneered by NETL-ORD since early 1990's**
  - Physics-based gas-solids flow Modeling
    - MFIX (Multiphase Flow with Interphase Exchanges)
    - Open source software http://mfix.netl.doe.gov
    - 2007 R&D 100 Award
  - Carbonaceous Chemistry for Computational Modeling (C_3M)
    - Detailed model for coal devolatilization, gasification and combustion reactions
    - Fuel flexibility (coal, biomass, and co-fired)
    - Patent application filed
    - 2008 FLC Tech Transfer Award
- **Extensive validation with data from Power Systems Development Facility (PSDF)**
  - Validation effort started in 2001
  - Bituminous, sub-bituminous and lignite coals under both air and oxygen blown conditions



Tech-Transfer Award 2006

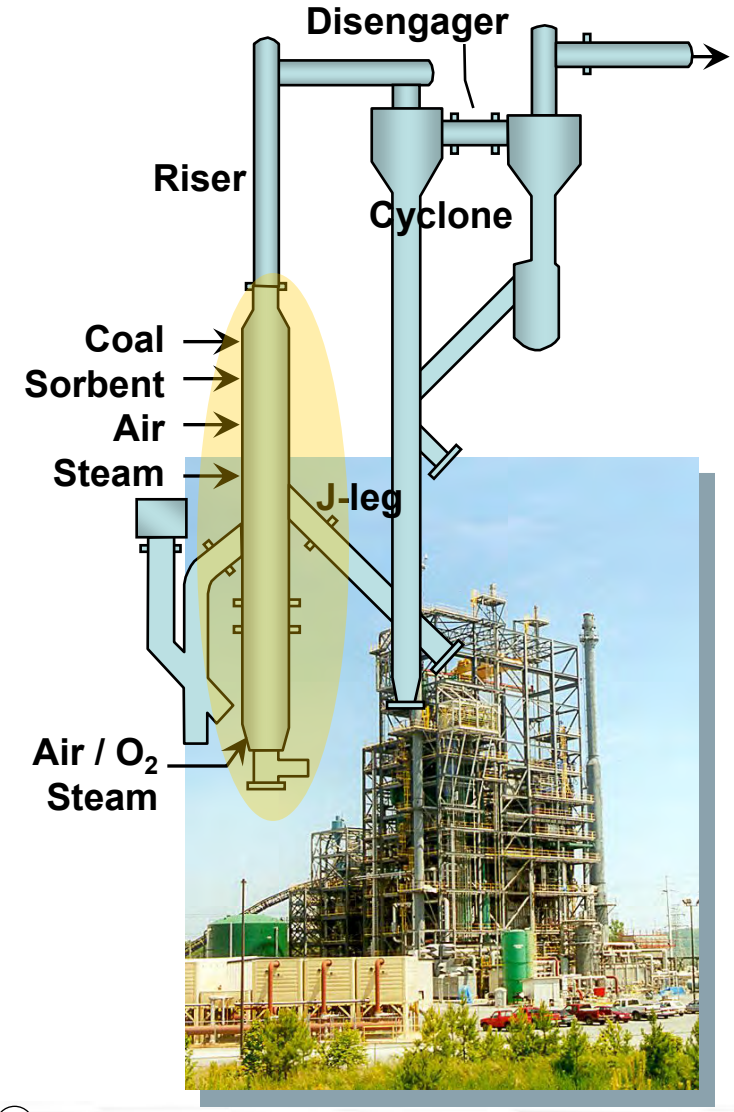
R&D100 Award 2007

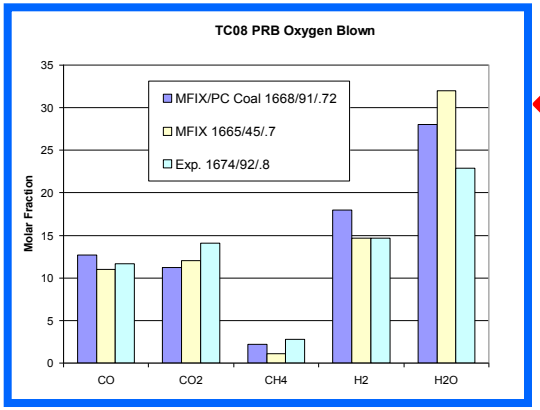


FEDERAL LABORATORY CONSORTIUM FLC FOR TECHNOLOGY TRANSFER

Excellence in Technology Transfer Award 2008

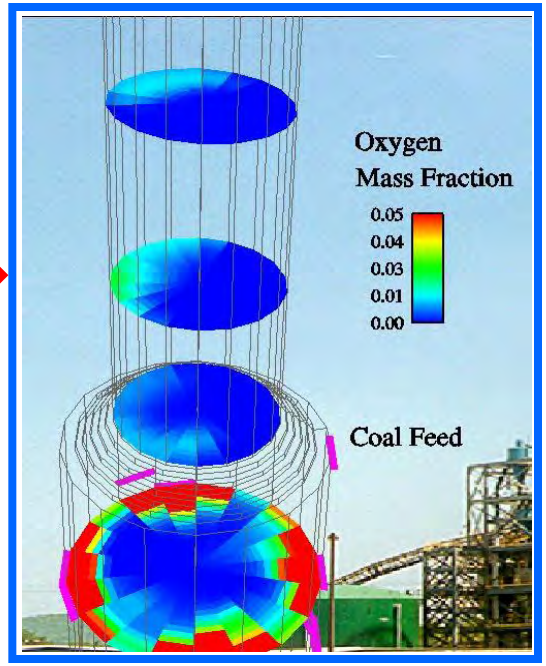
Model Validation with Pilot-scale Data

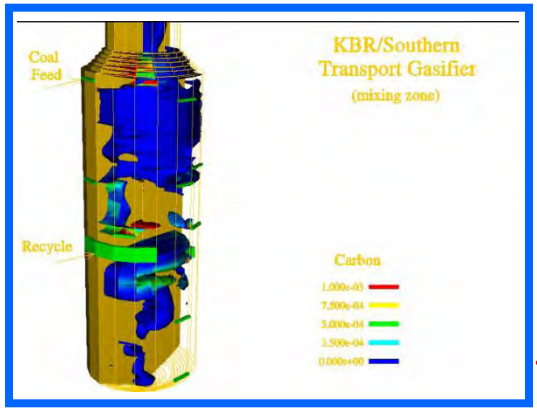




Comparison of predictions with pilot-scale data

Predicted oxygen breakthrough was later experimentally confirmed





Solids vol. fraction iso-surfaces colored by carbon mass fraction

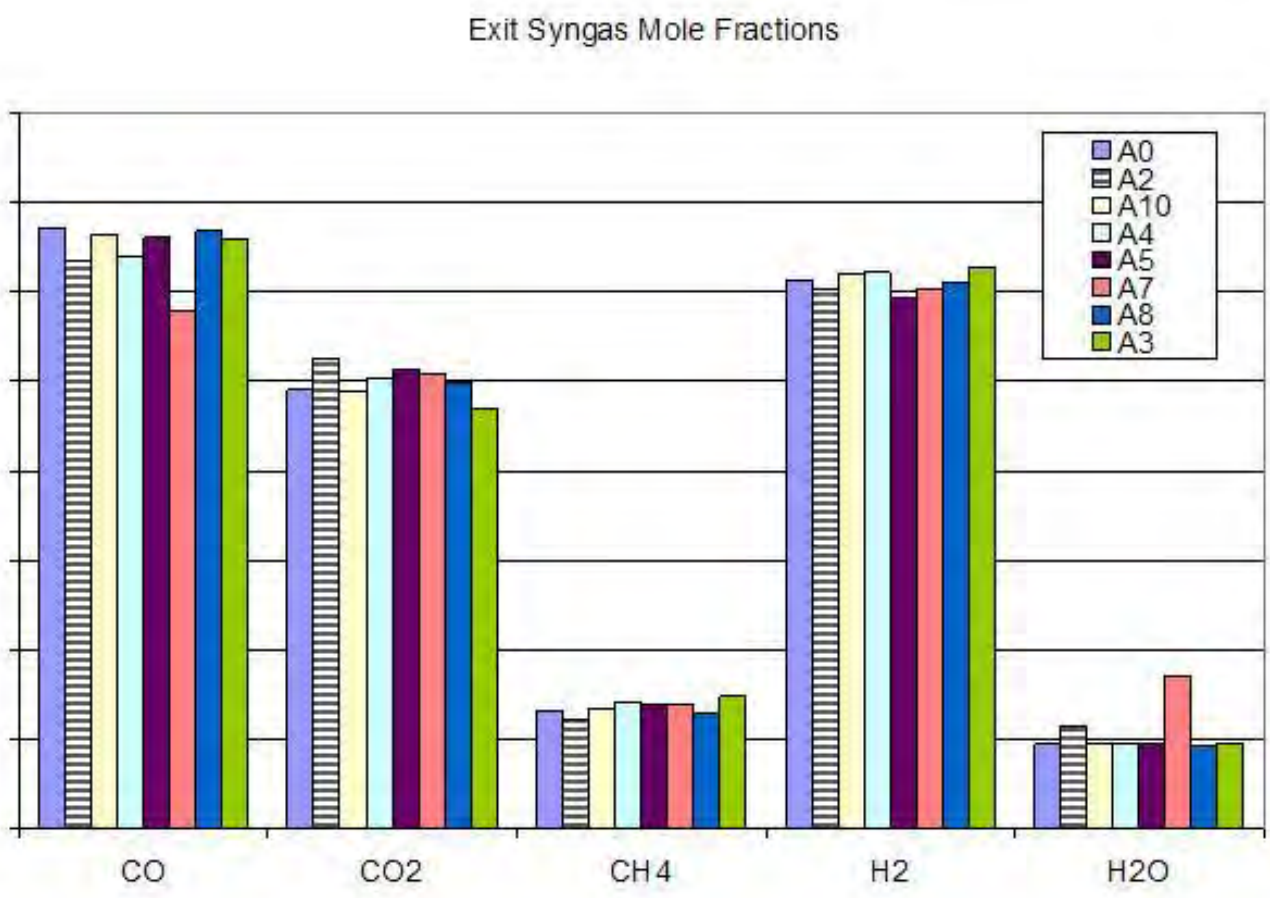
- C. Guenther, M. Syamlal, J. Longanbach, and P. Smith, Proceedings of the 20th Annual Pittsburgh Coal Conference, Pittsburgh, PA, September 15-19, 2003
- C. Guenther in Report on Workshop on Multiphase Flow Research, Morgantown, WV, June 6-7, 2006, http://tinyurl.com/c9r7ux

Commercial Scale TRIG (Transport Integrated Gasification)

- **Parametric studies requested by KBR for the commercial scale TRIG**
  - Effect of recycled syngas
  - Coal jet penetration (focus of an ongoing INCITE project)

- **Parametric studies requested by Southern Co. for the commercial scale TRIG**
  - Influence on gasifier diameter
    - L/D ratios 27,23,21,20
  - Influence on solids circulation rate
  - Influence on coal feed rate

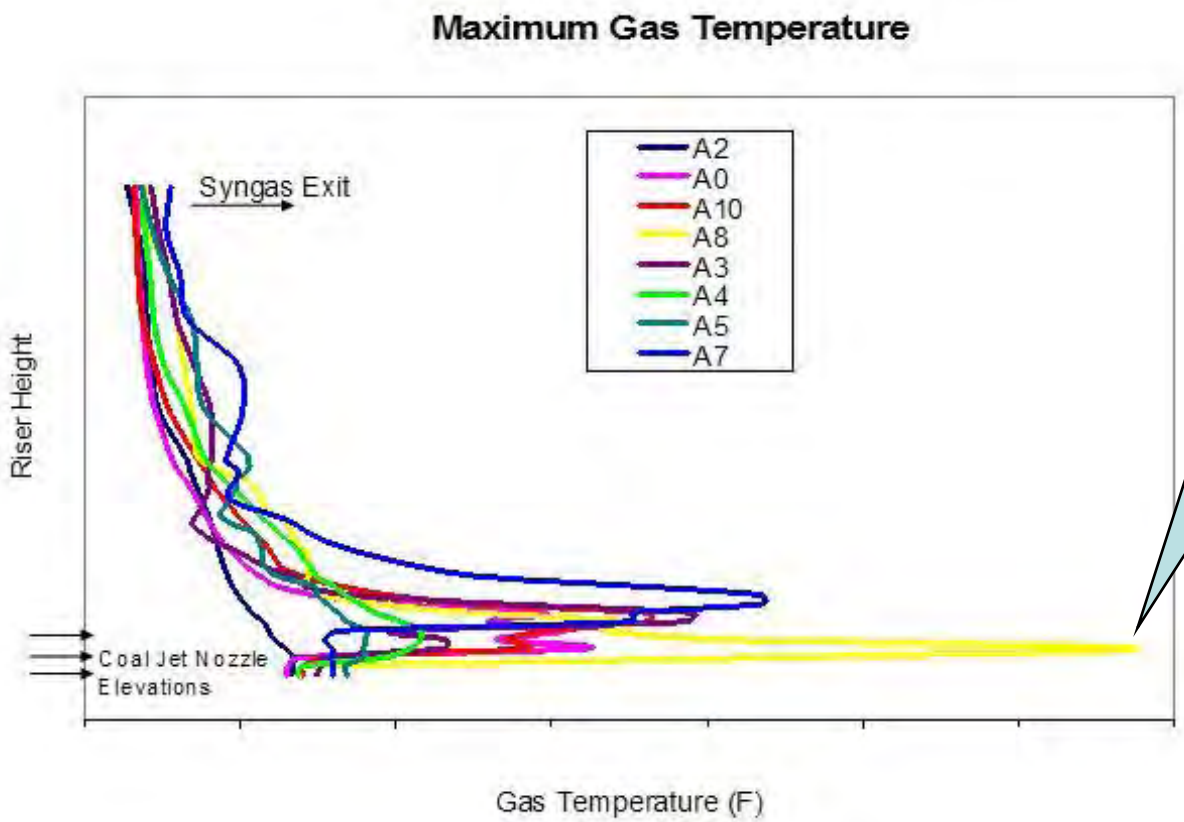
Predicted Commercial-Scale Syngas Composition

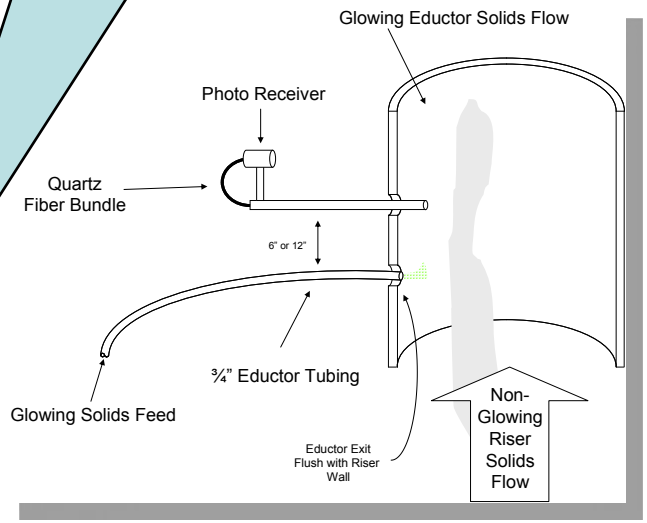


Mole fraction values removed

New Insight from Commercial Scale Gasifier Simulations

- Considerably higher peak temperature for certain cases!
- Led to further experimental investigation





Gas temperature values removed

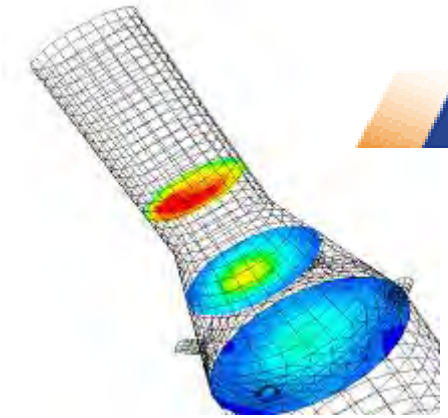
Reducing Cost and Time of Development

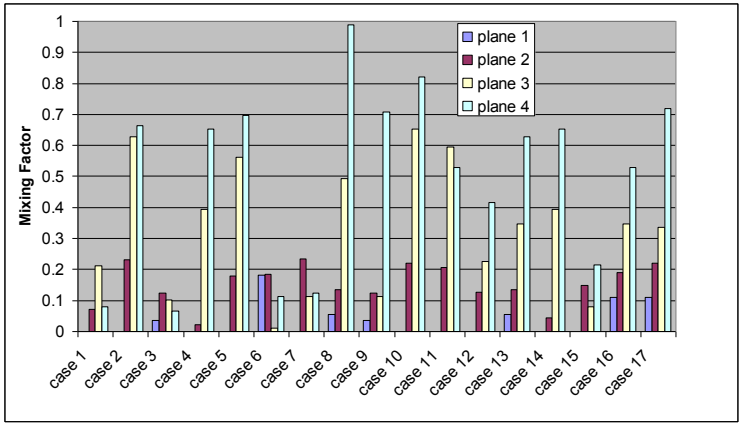
	Pilot-scale modification	
	Simulation	*Actual*
Time (wk)	*2*	*14*
Cost ($K)	*10*	*6000*

- **Discover designs unreachable by traditional methods**
  - e.g., improving coal jet design → eliminate high T regions → reduce operational problems → increase availability → reduce start up time by 3-10 years, saving $230-767 M ?
- **Get the design right the first time at every scale**
  - Avoiding rework could save months of downtime and the cost of rework ($63 M rough estimate based on “six-tenths rule”) ?
- **Skip building and testing at multiple intermediate scales**
  - Tens of millions of dollars and 3-5 years at every scale avoided
- **Learn from operations → Model as a knowledge repository**

Changing Design Paradigm: Design of Pilot-scale Hydrogasifier

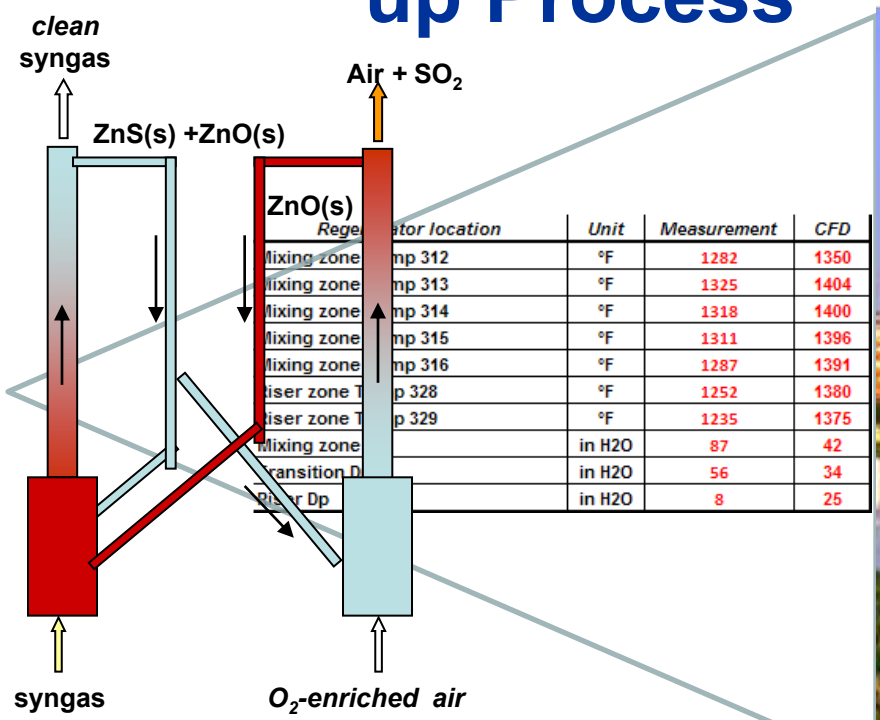
- **CFD model developed for the design of Arizona Public Service's Hydrogasifier**
  - Model based on C_3M, MFIX and Ansys/FLUENT
  - 17 simulations conducted based on different parameters: shooting angle, swirl, coal and H_2 feed rates, and nozzle ID
  - Statistical analysis of CFD results using solids flux and temperature as response variables
- **Final design parameters selected based on CFD analysis**
  - Large H_2 nozzle ID
  - 45° downward nozzle orientation
  - 30° degree swirl





Changing Design Paradigm: Scaling up RTI/Eastman Warm Gas Clean-up Process

0.3 MWe Unit at Eastman Chemical



Rege ator location	Unit	Measurement	CFD
Mixing zone mp 312	°F	1282	1350
Mixing zone mp 313	°F	1325	1404
Mixing zone mp 314	°F	1318	1400
Mixing zone mp 315	°F	1311	1396
Mixing zone mp 316	°F	1287	1391
Riser zone T p 328	°F	1252	1380
Riser zone T p 329	°F	1235	1375
Mixing zone	in H2O	87	42
Transition D	in H2O	56	34
Riser Dp	in H2O	8	25

50 MWe Unit scheduled for commissioning in 1Q FY 2012 at Tampa Electric, Polk Power station

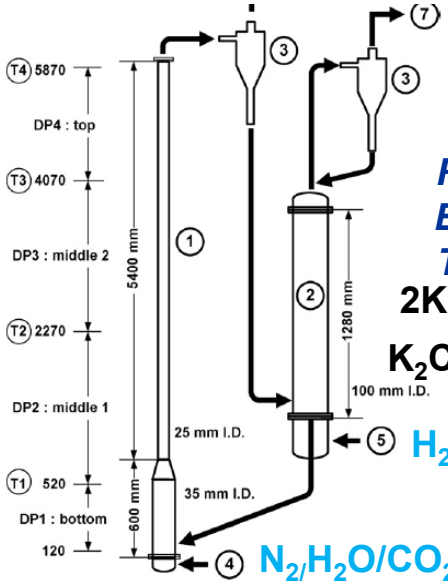
- **Transport Desulfurizer Model being validated with data from the 0.3 MWe Eastman Unit**
- **Validated model will be used for scaling up to 50 MWe**

Changing Design Paradigm: Evaluating Conceptual Designs

Absorption Riser

Absorption Fast Fluidized Bed
T ≈ 330-360 K

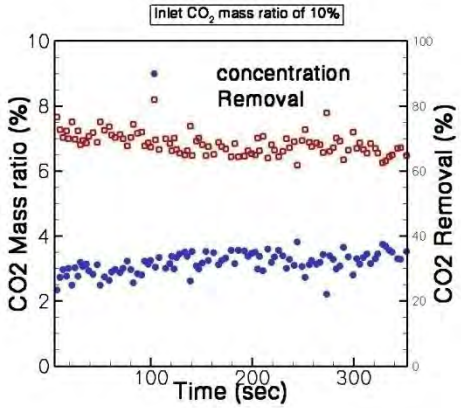
$K_2CO_3 + CO_2 + H_2O \rightarrow 2KHCO_3 + heat$



Regeneration Bubbling Bed
T ≈ 390-490 K

$2KHCO_3 + heat \rightarrow K_2CO_3 + CO_2 + H_2O$

Yi et al. (2007)



✓ Predicted 60-80% removal rate of CO_2 comparable to data

Pressure drop (mm H_2O)	Simulation	Yi et al.(2007)
DP1	114	100
DP2	423	500
DP3	413	200
DP4	370	70

Simulation Results

- **CO_2 capture reactor model being validated with lab-scale data from Korea Institute of Energy Research (KIER)**

Changing Design Paradigm: Evaluating Conceptual Designs

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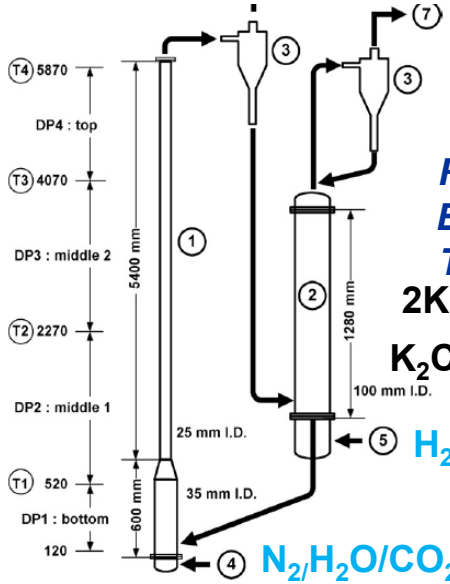

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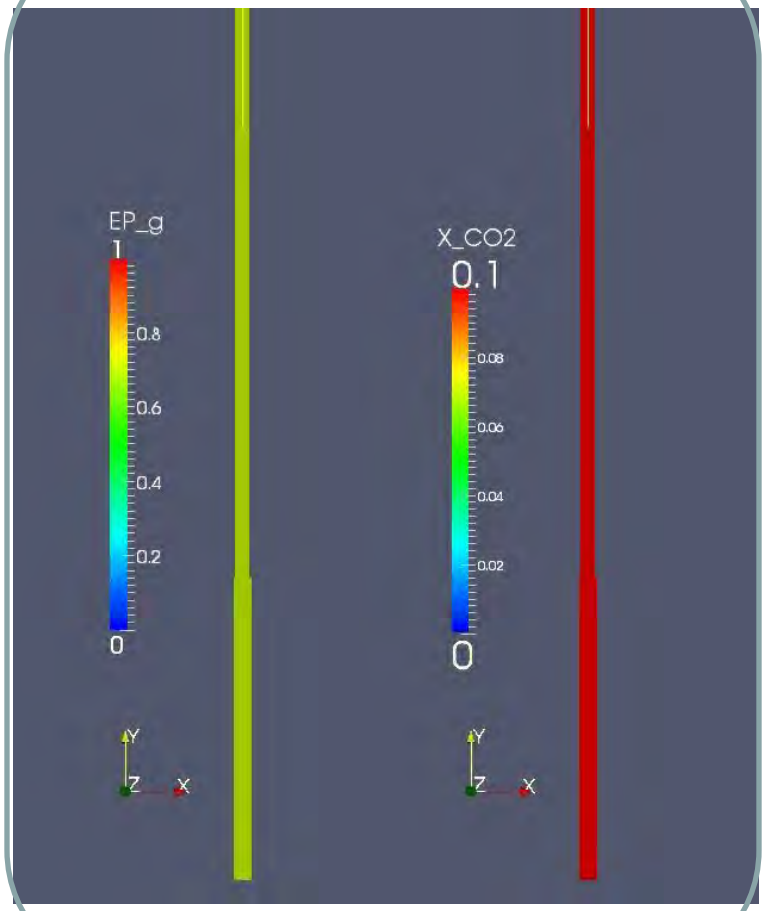
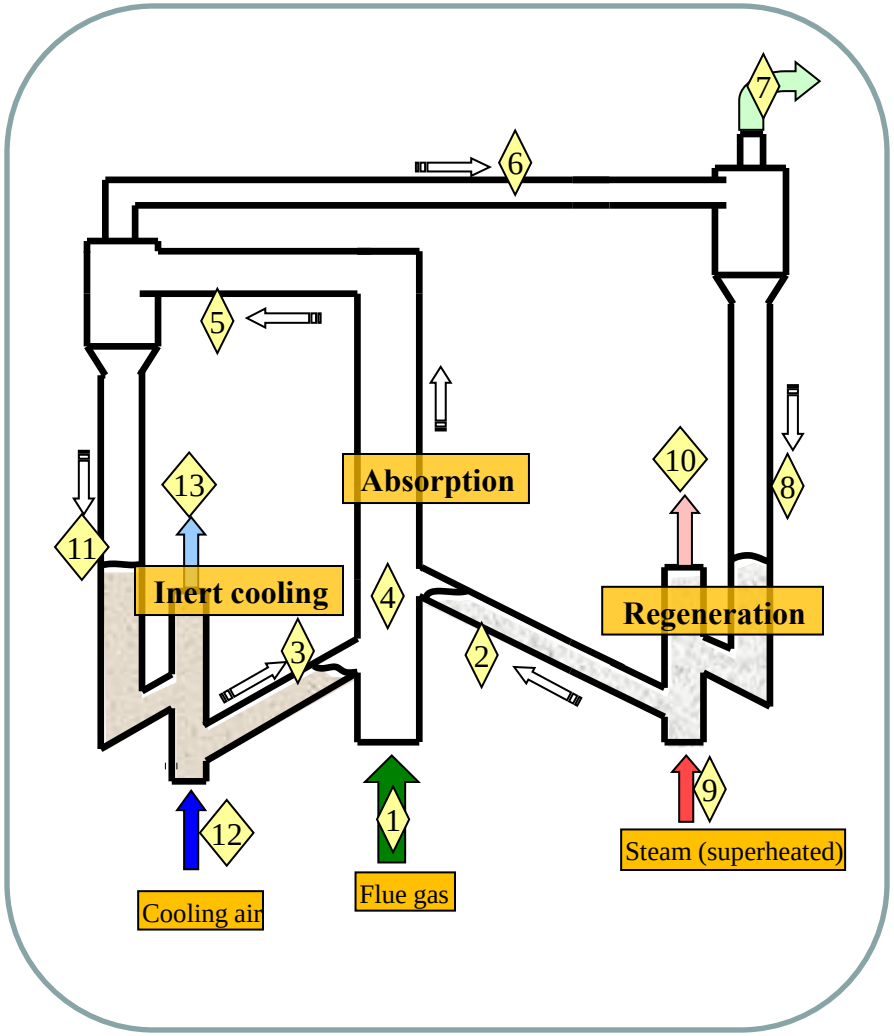


- The animations show void fraction and CO_2 mass fraction distribution in the absorber

Changing Design Paradigm: Evaluating Conceptual Designs

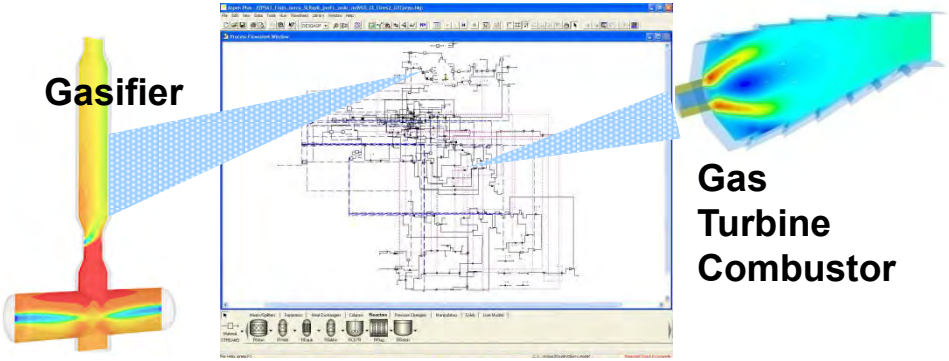
- Evaluate conceptual designs of NETL design for absorber heat management (patent pending)
  - Optimal sorbent and inert particle sizes and densities
  - Reactor configurations
- Validate the model with data from NETL-KIER Experiments
  - Test NETL sorbent (patented) in KIER Reactor
  - Calibrate the reaction kinetics in CFD model for NETL Sorbent



APECS: Optimize operating strategy

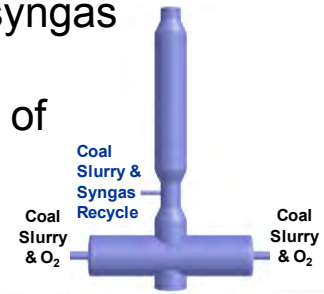
Power & Hydrogen Production with CO_2 Capture

- **Process Simulation**
  - Aspen Plus® steady-state
  - All major plant sections
  - Over 250 unit ops

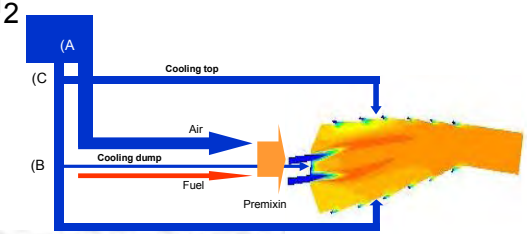


APECS Co-Simulation of Polygeneration Plant

- **CFD Simulations**
  - Entrained-Flow Gasifier
    - FLUENT® 3D/ROM
    - Accurate calculation of synthesis gas composition
    - Embedded in syngas recycle loop
    - Optimized flow of coal slurry and syngas recycle to 2nd stage



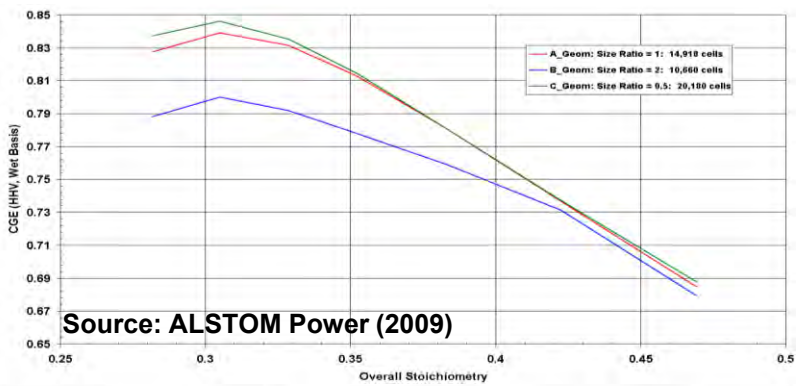
  - Gas Turbine Combustor
    - FLUENT® 3D/ROM with partially pre-mixed combustion
    - Accurate calculation of GT inlet temperature
    - Embedded in design spec loop to determine power/H_2 production
    - Optimized cooling strategy to minimize NO_x



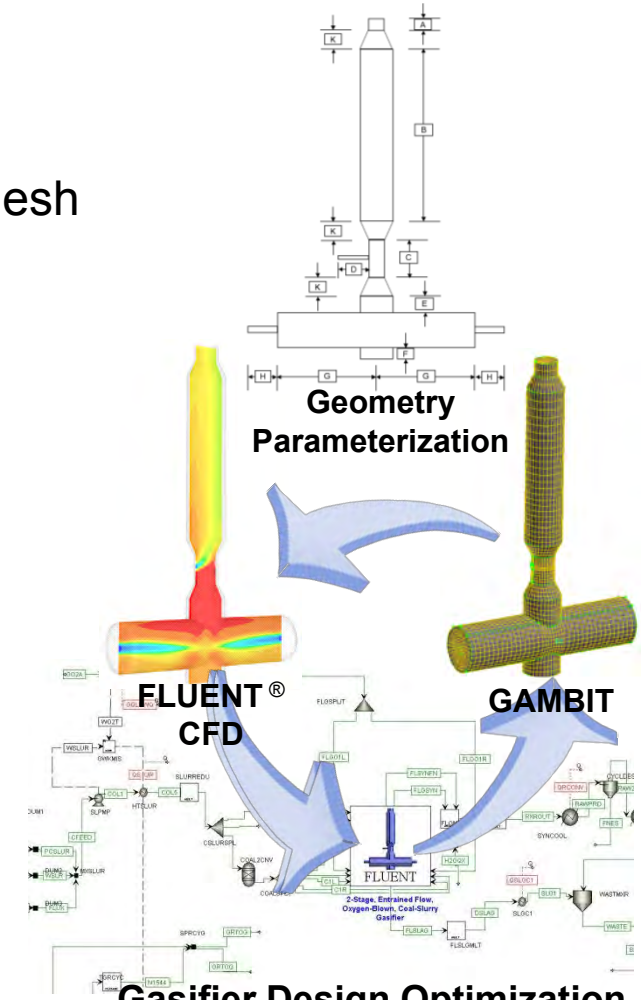
APECS: Optimize Geometric Design

Entrained-Flow Gasifier Design

- Geometry parameterization within process simulation via CAPE-OPEN parameters
- Automated regeneration of CFD geometry/mesh
  - GAMBIT => FLUENT® => Aspen Plus®
- Case study: Gasifier design optimization
  - Geometry and inlet cross-sections scale with coal throughput in order to preserve cross-sectional velocities and residence times
  - Vary oxygen flow rate to maximize cold gas efficiency (CGE) for a given coal throughput



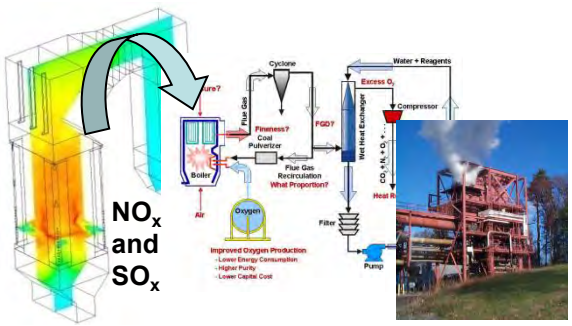
Source: ALSTOM Power (2009)



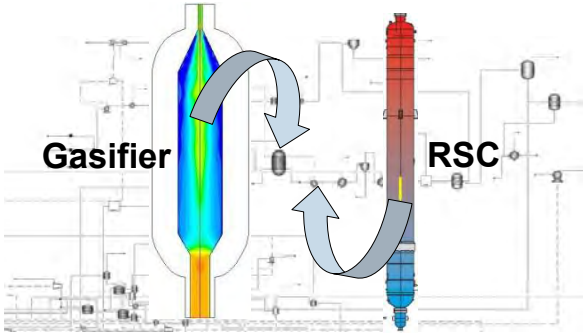
Gasifier Design Optimization in Aspen Plus®

APECS Application Projects at ALSTOM Power

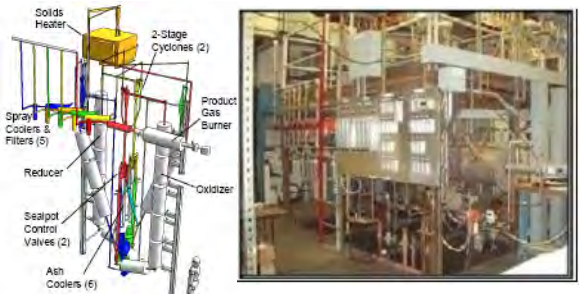
- **Oxy-Combustion**
  - 18 MW_{th} Boiler Simulation Facility (BSF)
  - BSF island (gas side only) with flue gas recycle (FGR)
  - FLUENT® 3D CFD boiler with pollutant species (NO_x, SO_x) exposed to Aspen Plus® via CAPE-OPEN parameters
  - Characterize impact of various FGR and cleanup scenarios on pollutant emissions for candidate BSF configurations
- **IGCC with CO_2 Capture**
  - 556 MW_e IGCC simulated in Aspen Plus®
  - FLUENT® CFD models
    - Single-stage, downward-fired, coal-fed, entrained-flow gasifier
    - Radiant syngas cooler (RSC)
  - Transfer multi-dimensional boundary conditions
  - Analyze integration of gasifier and RSC
  - Optimize heat integration with overall plant
- **Chemical Looping Combustion**
  - APECS co-simulation of 65 kW_{th} pilot-scale facility
  - FLUENT® 3D CFD/ROMs for solid fuel and air reactors
  - Dense, multiphase flow using E-E solution



ALSTOM: Oxy-Combustion



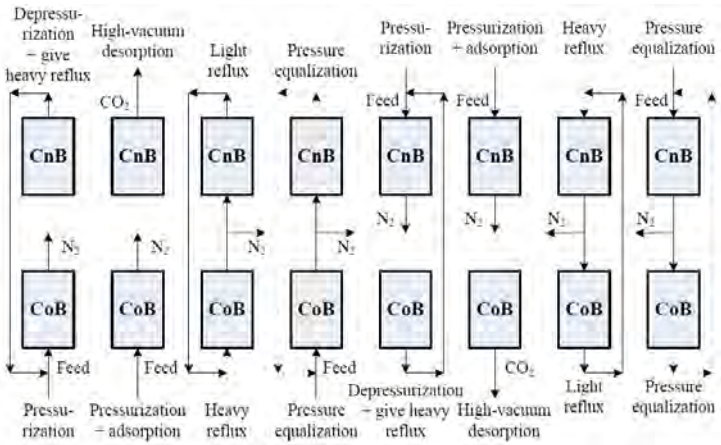
ALSTOM: IGCC with CO_2 Capture

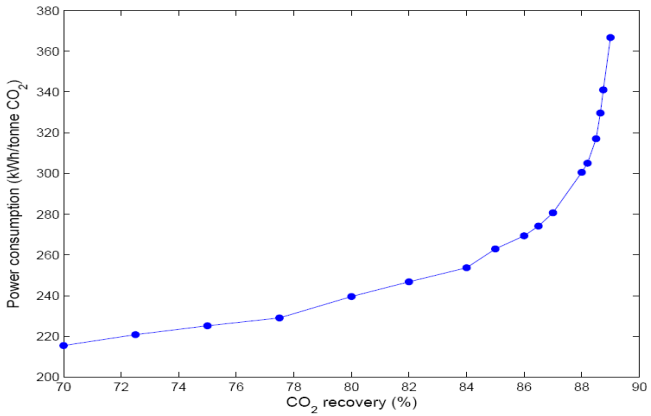


ALSTOM: Chemical Looping Combustion

Optimal Design of Pressure Swing Adsorption (PSA) Cycles for Pre- and Post-Combustion CO_2 Capture

- Systematic methodology to develop, evaluate, and optimize PSA cycles for high purity pre- and post-combustion CO_2 capture
  - Maximize CO_2 recovery for a given purity
  - Maximize feed throughput
  - Minimize power requirement for a given level of CO_2 purity and recovery
- Optimal sequence of operating steps is achieved through the formulation of an optimal control problem
  - Partial differential algebraic equation (PDAE)-based model of the PSA system and the cyclic steady state condition
- Approach is very promising and useful for evaluating the suitability of different adsorbents, feedstocks, and operating strategies for PSA, and assessing its usefulness for CO_2 capture





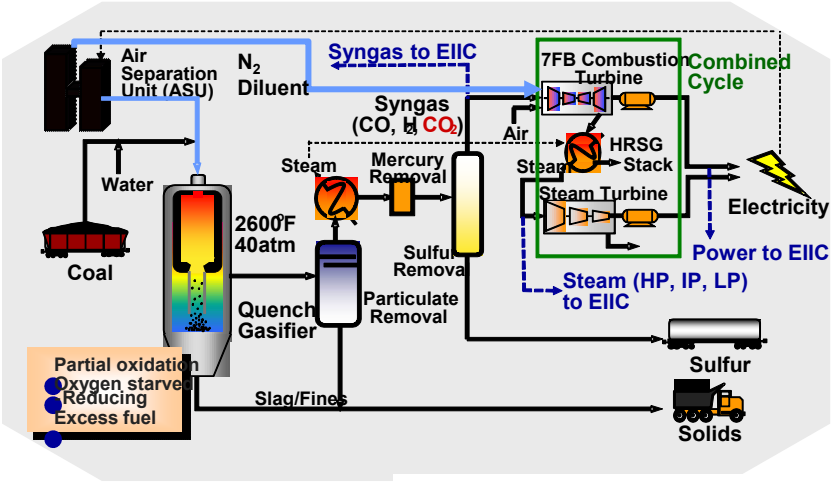
Agarwal, A., L.T. Biegler, and S.E. Zitney, "Superstructure-Based Optimal Design of PSA Cycles for Post-Combustion CO2 Capture," Proc. of the 26th Annual International Pittsburgh Coal Conference, September 21-24, Pittsburgh, PA (2009).

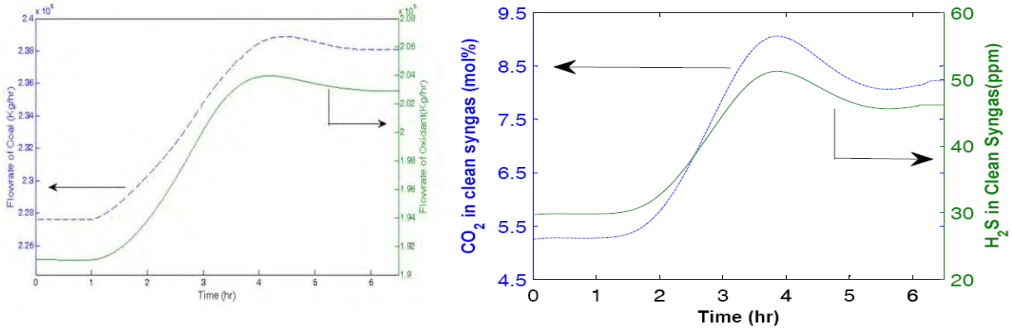
Vetukuri, S., A. Agarwal, L.T. Biegler, and S.E. Zitney, "Optimal Design of PSA Cycles for Pre-Combustion CO2 Capture Using a Superstructure-Based Approach," Proc. of the 26th Annual Int'l Pittsburgh Coal Conference, September 21-24, Pittsburgh, PA (2009).

Plant-wide IGCC Dynamic Simulation

Operability and Control Analysis

- Dynamic simulation and control of plant-wide IGCC with CO_2 capture
- Detailed dynamic models
  - Elevated-pressure air separation unit (ASU)
  - Entrained-flow gasifier
  - Claus plant
  - Dual-stage Selexol for H_2S and CO_2 removal
  - Combined cycle
- Aspen Dynamics® pressure-driven simulation with more than 250 unit operations
- Performing operability studies and analyzing control strategies





Response to a 5% ramp increase in coal feed flow rate

Bhattacharyya, D., R. Turton, and S.E. Zitney, "Plant-wide Dynamic Simulation of an IGCC Plant with CO2 Capture," Proc. of the 26th Annual International Pittsburgh Coal Conference, September 21-24, Pittsburgh, PA (2009).

Bhattacharyya, D., R. Turton, and S.E. Zitney, "Plant-wide Dynamic Simulation of an IGCC Plant with CO2 Capture," Presented at 2009 AspenTech Worldwide User Conference, May 4-7, Houston, TX (2009).

NETL's IGCC Dynamic Simulator Research and Training Center

- **Plant-wide IGCC dynamic simulator**
  - Generic IGCC plant with CO_2 capture
  - Full-scope operator training simulator (OTS)
    - IGCC plant start-up, shutdown, normal and faulted operations as well as safety and risk analysis
    - Full DCS emulation and control strategy analysis
    - Instructor capabilities, scenarios, trending, etc.
  - Immersive training system (ITS)
    - Real-time, 3D, immersive, interactive virtual environment for training plant engineers and outside field operators
- **NETL Collaboration Partners**
  - Universities: WVU, CMU, Pitt
  - Software: Invensys Process Systems
  - Core Consultants: FCS, Enginomix, EPRI
  - CoalFleet: AEP, BP, Doosan, GRE, Southern
  - External Consultants: Gasification Solutions, Energy Resources Consultancy, Gas Processing Solutions, TECO-Polk, Robertson-Bryan, Inc.
- **Deployment Status**
  - OTS deployment in 3-4QFY10
  - ITS deployment in 1QFY11

(Courtesy of Invensys Process Systems)

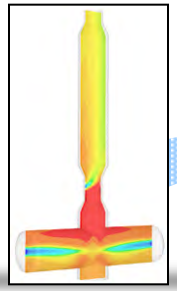
Provost, G.T., H.P. Stone, M. McClintock, S.E. Zitney, E. Liese, R. Turton, D. Bhattacharyya, M. Quintrell, and J. Marasigan, and M.E. Erbes, "NETL to Establish Dynamic Simulation Research and Training Center for Demonstration of IGCC Technology with CO2 Capture," Proc. of the 26th Annual International Pittsburgh Coal Conference, September 21-24, Pittsburgh, PA (2009).

Zitney, S.E., R. Turton, M.E. Erbes, H.P. Stone, G.T. Provost, M. McClintock, M. Quintrell, and J. Marasigan, "NETL to Establish Dynamic Simulation Research and Training Center to Promote IGCC Technology with CO2 Capture," Proc. of the COAL-GEN 2009 Conference, August 19-21, Charlotte, NC (2009).

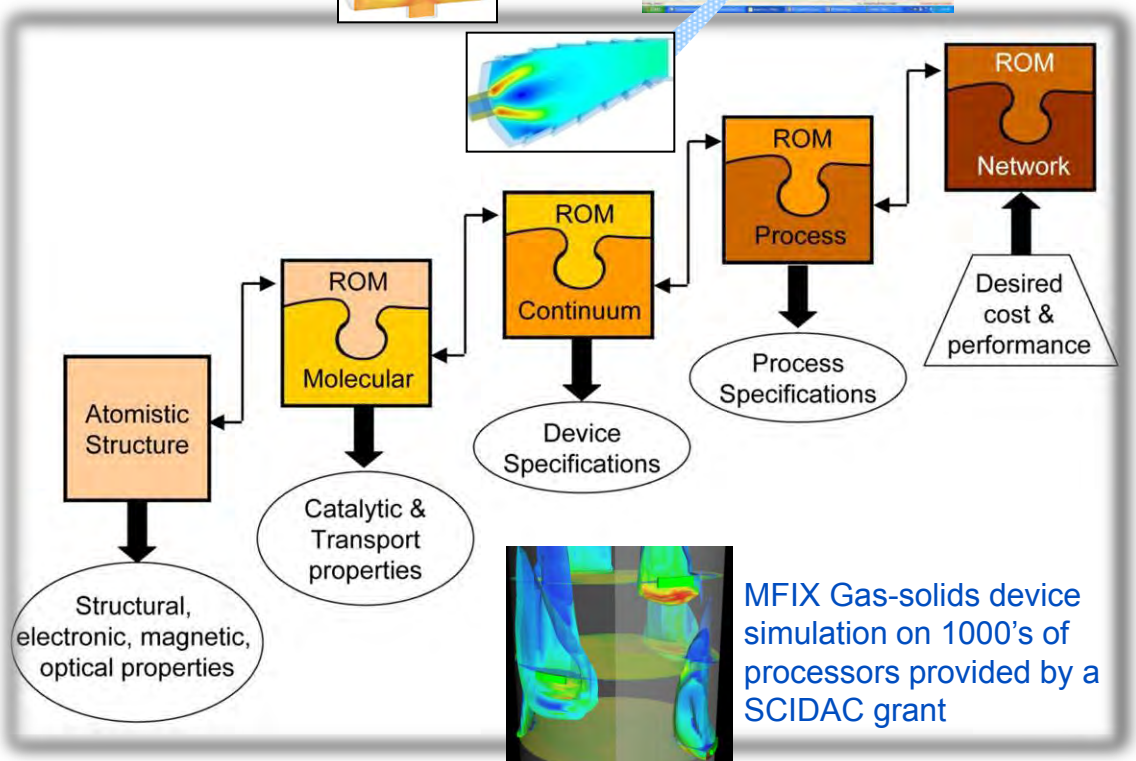
How can we increase the fidelity of models?

- **Fidelity of models at each scale depends upon submodels representing physical phenomena at a lower scale; for example,**
  - Force fields in MD simulations of ionic liquids
  - Gas-solids drag or solids stress in CFD models
  - Equilibrium Reactor in process models
- **They are: assumptions, derived from experiments at a lower-scale, based on analytic models of the lower-scale phenomena, or formulas adjusted to fit experimental data at the current-scale**
- **The appropriate level for demonstration is at the scale when empirical information in the models may require recalibration**
- **Recalibration at intermediate scales can be avoided by making the models more and more physics-based, which is the idea behind multi-scale modeling**

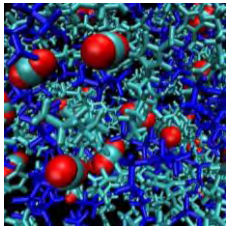
CO_2 Capture Simulator?



APECS simulation of poly-generation plant with carbon capture includes CFD models of turbine combustor and gasifier



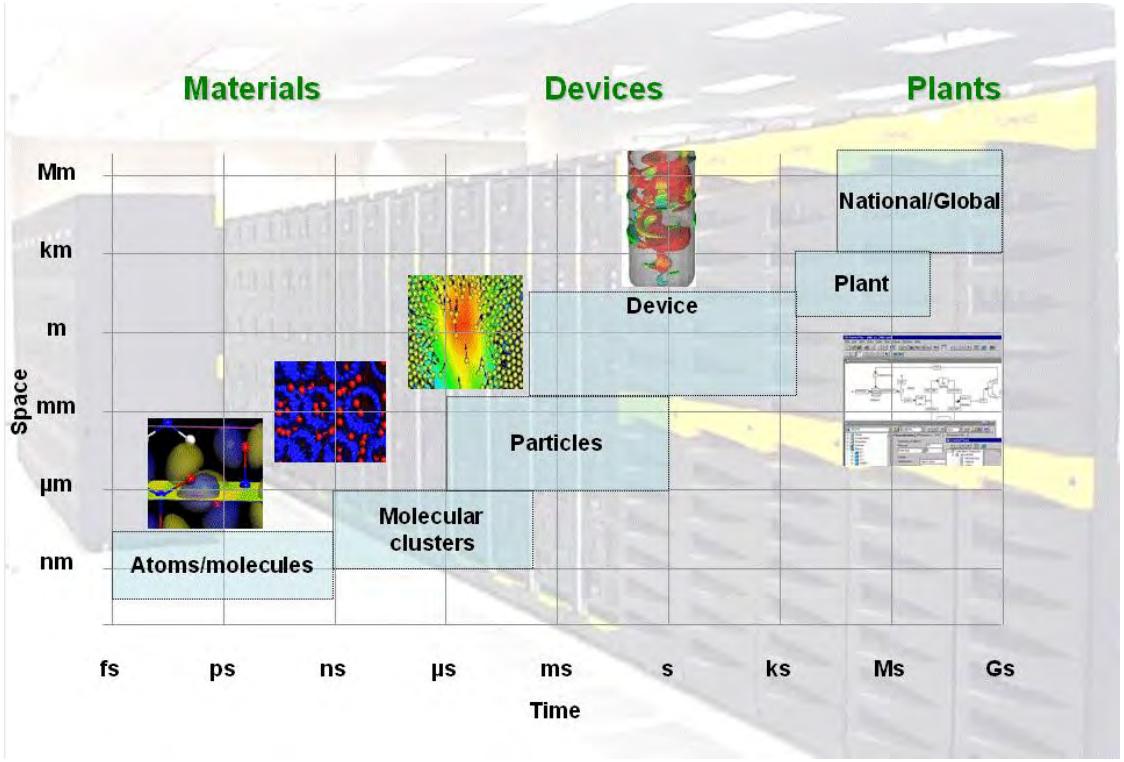
Computational screening of capture materials:
- ionic liquids
- solid sorbents



MFIX Gas-solids device simulation on 1000's of processors provided by a SCIDAC grant

Linking models at various scales using reduced order models (ROM) and deriving lower-scale specifications through an inverse optimization formulation.

The Research Challenge



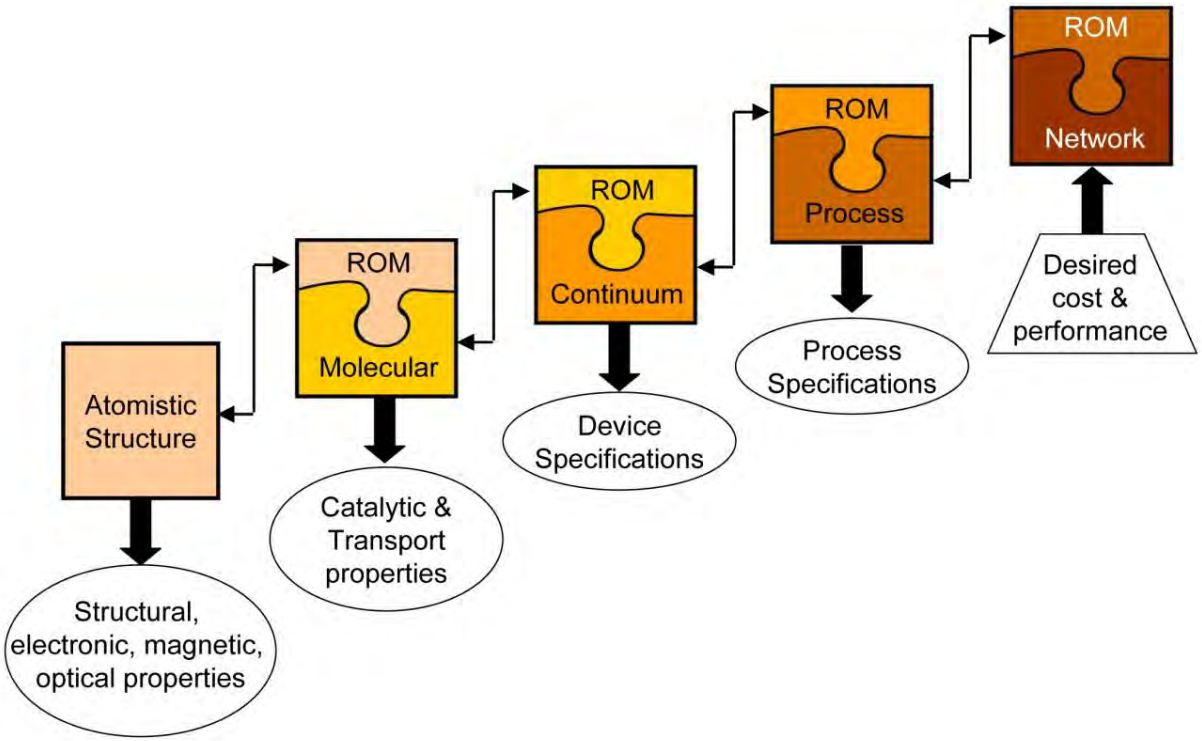
<u>Time and Length Scales cover over 15 orders of magnitude</u>

- **Reflect behavior from atomistic levels to process units and networks**

<u>Strongly coupled</u>

- **Components at smaller scales provide building blocks for scales above**
- **Demands at larger scales impose specifications below**

Proposed Integration Approach



- Detailed, Precise and Computationally Expensive Models at All Levels
- Construction of Reduced Order Models (ROMs) allow model interaction
- ROMs must be validated and verified over application domain
- ROM Approximation Errors must be bounded and quantified
- Integration among ROMs effected through a large-scale optimization framework

Reduced Order Models

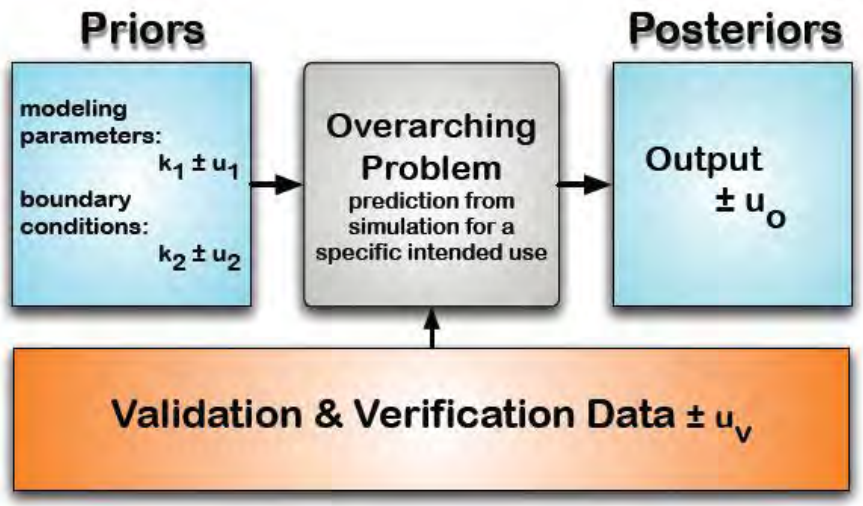
Levels of ROMs

- *Process Level* - Analytic models are derived from simplified, limiting behaviors of transport, reaction and equilibrium phenomena and conservation laws, e.g., macroscopic models for rate laws, vapor liquid equilibrium and thermodynamic properties
- *Device level,* proper orthogonal decomposition (POD), variable resolutions models on meshes with varying degrees of refinement, variable-fidelity physics models (e.g. inviscid, irrotational, incompressible flow).
- *Atomistic and molecular levels*, infer thermodynamic and kinetic properties and constants and regress to physics-based ROMs.
- General regression-based model are derived that apply data-driven regression approaches (e.g., PCA, compresssed sensing, neural nets, wavelets).

Open questions and research challenges:

- Efficient, systematic ROM development at all length and time scales
- Verification and validation of ROMs both with limits on performance and bounded uncertainties (e.g., statistically derived confidence regions)
- Development of large-scale optimization formulations that incorporate the limitations of the ROM and the uncertainty description

Quantifying Uncertainty



(From Phil Smith, U. of Utah)

Formal methodology for producing upper and lower error bounds on simulations with quantified uncertainty based on experimental observations.

- Integrate computational and experimental data to quantify predictivity of reduced order model
- Quantify uncertainty in model parameters, boundary conditions, numerical uncertainty and experimental uncertainty.
- Assess sensitivities of the output function to the input uncertainties
- Using candidate approximate models, develop quantified uncertainty in resulting output function ($u_{lower} < E < u_{upper}$).
- Provide level of confidence in decision implementation and optimization

Optimization

Enabling "glue" for integration of multi-scale modeling and decision-making

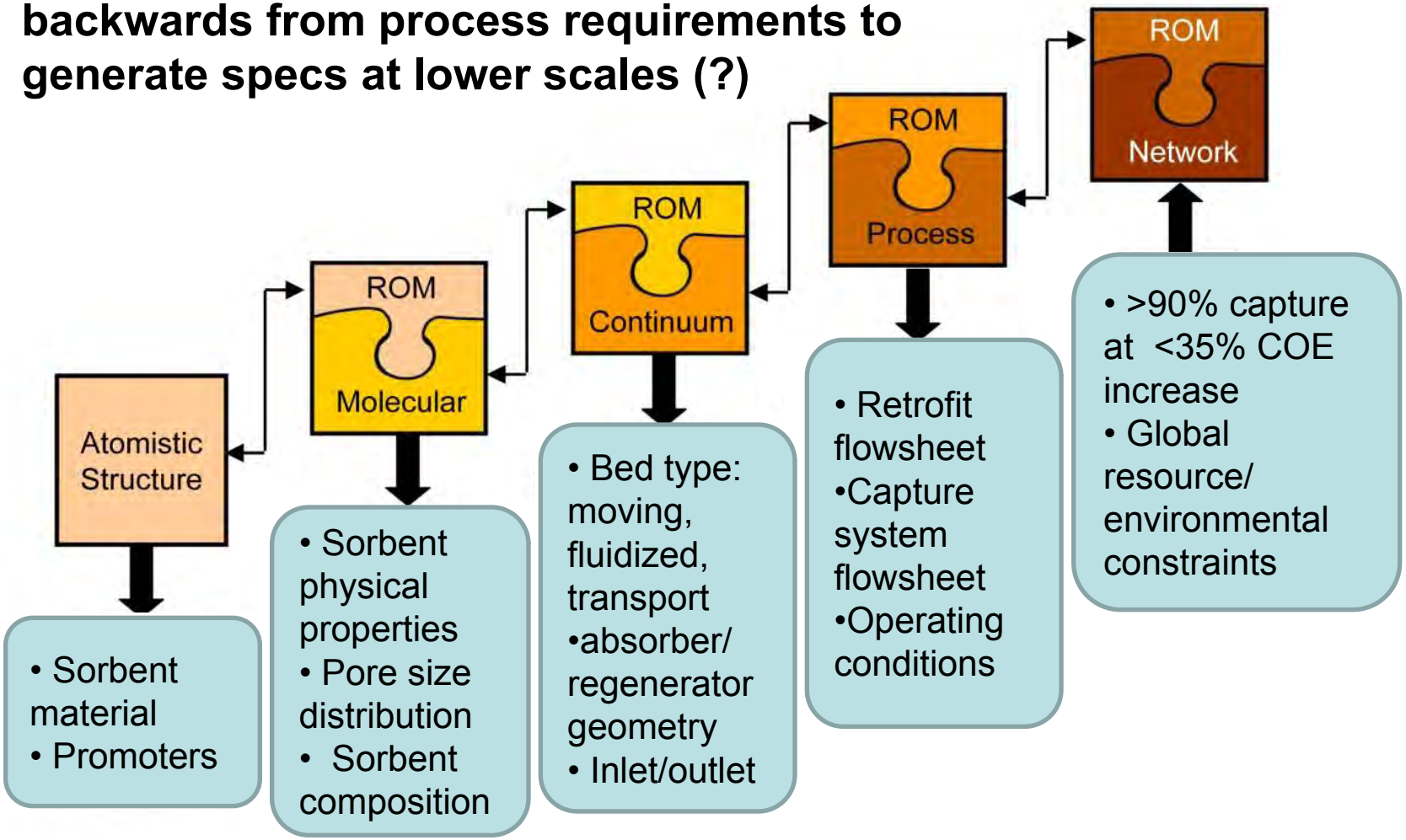
- Link ROMs and their uncertainty bounds to high-level models
- Decomposition levels and over-approximation strategies
- Trust region-based strategies for ROM adaptation
- Very efficient large-scale open optimization environments and algorithms
- Continuous optimization (local) – millions of variables, thousands of degrees of freedom, linear complexity
- Mixed integer optimization – both discrete and continuous optimization with thousands of variables
- Global optimization – guaranteed global solutions in logistics, bio-informatics, large-scale planning

Multi-scale optimization <==> Optimization under uncertainty:

- **Deterministic models and ROMs with two uncertainty types: randomness and limited knowledge**
- **Leads to optimal solutions that**
  - Incorporate all multi-scale information
  - Robust to ROM uncertainty bounds
  - Adapt ROMs to changing input conditions

CO_2 capture simulator requirements

- **Reverse the flow of information to reason backwards from process requirements to generate specs at lower scales (?)**



Questions ?

Gordon E. Moore, Electronics, Volume 38, Number 8, April 19, 1965

This cartoon appeared in a 1965 article by Gordon Moore, co-founder of Intel, which contained the observation now well known as Moore's Law.

For Additional Information

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www.netl.doe.gov

Office of Fossil Energy

www.fe.doe.gov