DE-FE0031522: Advance Syngas Cleanup for Radically Engineered Modular Systems (REMS)

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Small-Scale Modularization of Gasification Technology Components for REMS – Objectives of the FOA

• DOE's Clean Coal Program is focused on developing advanced technologies that increase the performance, efficiency and availability of existing and new coal-fueled power generation

• Develop emerging gasification technologies that can be scaled down to modular small-scale (1-5 MW) via the Radically Engineered Modular Systems (REMS) concept

• Develop REMS process technologies that are cost effective relative to SOTA commercial technology, due to low cost fabrication via advanced manufacturing

• REMS-based combined heat and power or polygeneration system implemented in remote areas subjected to traditionally high energy costs

**Project Objective:** Develop modular sorbent-based warm syngas cleanup designs that will enable 1- to 5-MW REMS-based plants utilizing all of our abundant domestic coal reserves to be cost-competitive with large state-of-the-art commercial plants.
**Objective:** Develop modular sorbent-based warm syngas cleanup designs that will enable 1- to 5-MW REMS-based plants utilizing all of our abundant domestic coal reserves to be cost-competitive with large state-of-the-art commercial plants.

- Build on the extensive development work of RTI’s Warm-gas Desulfurization Process (WDP)
- Study desulfurization performance of WDP sorbent for low-sulfur syngas streams
- Develop a fluid-bed regenerator for REMS application, especially with low-sulfur syngas
- Develop a fixed-bed sorbent and process for its inherent suitability for small-scale modularized systems
- Develop and optimize conceptual designs for desulfurization processes based on fluidized-bed and fixed-bed reactors
A unique process technology based on dual transport reactor loops (similar to FCC reactor designs)…

Enables high removal of total sulfur (≥99.9%) from syngas at temperatures as high as 650° C.

… and on a regenerable, high-capacity, rapid acting, attrition-resistant sorbent.

RTI Proprietary Desulfurization Sorbent
- R&D 100 Award
- Unique highly-dispersed nanostructures
- Developed in long-term cooperation with Clariant (~100 tons to date)
- Covered by extensive US & International patents, including several recent improvements
Technology Development Timeline

Invention (2001)


Demonstration at TECO, Tampa, FL (2010-2016)

- Eastman Chemical Co., TN: 3000 hr, coal-derived syngas
- RTI, NC: Concept proven & modeled
- Proprietary RTI sorbent
- R&D 100 Award (2004)

- 50 MWe equivalent scale, coal/petcoke-derived syngas
- $168.8MM DOE funding to design, construct, operate
WDP Potential to Address REMS FOA Objectives

Key Strengths of WDP still apply

- Rapid reaction rates of desulfurization and regeneration
- Proven material chemistry and scale-up
- Fundamentally applicable to any sulfur concentration and pressure
- Modular design expected to reduce capital costs over other technologies
- Anticipate similar energy savings and GHG reductions as large-scale

Knowledge gaps for application

- Expanded experimental data for low-sulfur syngas
- Identify modifications to the current process configurations to enable deployment of modular, cost-competitive cleanup systems
- Hydrodynamic data for fluid bed regenerator
- Processing steps to yield fixed-bed extrudate
- Performance of extrudates for fixed-bed
- Techno-economic assessment for REMS

How does this technology development apply to REMS & low-sulfur coals?
Framework for Project

Extended WDP sorbent testing towards low-sulfur syngas (Tasks 2) (Complete)

Fixed-bed process for low-sulfur syngas (Task 4) (Complete)

Modified fluidized-bed process for low-sulfur syngas (Task 3) (Complete)

Process Modeling and Techno-Economic Assessments (Task 5) (75% complete)

Key Focus Areas
• Project milestones on track
• On track with all the technical and financial reporting requirements
• Investigating commercial interest in the fixed-bed process
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1 This value is based on values provided in DOE/NETL’s “Cost and Performance Baseline for Fossil Energy Plant Volume 3a: Low Rank Coal to Electricity IGCC Cases (DOE/NETL2010/13990) which have been updated for 2016 costs.
Task 2.0: Low-Sulfur Testing

- Objective: Study desulfurization performance of WDP sorbent for low-sulfur syngas streams
- Commercially available fluidizable WDP sorbent was used for testing
- Testing performed in our existing Bench-Scale Fluidized-Bed Sorbent Testing System and atmospheric pressure TGA
- Parametric testing covered the typical operating conditions of temperature, pressure, syngas composition, and residence time
- Results validated the excellent performance of sorbent even under low-sulfur syngas conditions
- Task 2 and Milestone 3 completed
Atm-TGA and Bench-Scale Sorbent Testing System

- Sorbent testing in simulated syngas and oxidation gases
- Operates at atmospheric pressure and up to 700°C
- Utilizes 5 to 20 mg of sorbent material
- Cross flow operation allows for kinetic measurements

- Sorbent testing in simulated syngas and oxidation gases
- Operate up to 40 barg and 700°C
- Utilizes 100-300 g material
- Suspended quartz reactor inside stainless steel pressure vessel
Equilibrium Sorbent Sulfur Loading

- Tested performance of fluidizable RTI-3 sorbent under varying operating conditions – temperature, pressure, \( \text{H}_2\text{S} \) concentration and syngas composition
- Generated the desired low-sulfur syngas sorbent performance database and quantified the variation in equilibrium sorbent capacity as a function of changing test conditions
- Sorbent remained stable over multiple cycles and varying test conditions
A simplified kinetic expression was generated to incorporate the effect of adsorption operating parameters (temperature, $\text{H}_2\text{S}$ partial pressure, etc.)

Excellent agreement was observed between the experimental and model-predicted data.

\[
\frac{q_t}{q_e} = 1 - \exp \left\{ - \left[ C_1 \text{P}_{\text{H}_2\text{S}} \exp \left( \frac{-E_A}{RT} \right) t \right]^{C_2} \right\}
\]
A simplified kinetic expression was generated to incorporate the effect of regeneration operating parameters (temperature, $O_2$ partial pressure, etc.)

Excellent agreement was observed between the experimental and model-predicted data

\[
q_t = q_e \exp \left\{ - C_1 \exp \left( \frac{-E_A}{RT} \right) t \right\}^{c_2}
\]
Task 3.0: Fluid-Bed Regenerator Development

- Objective: Development of a fluid-bed regenerator for REMS application, especially with low-sulfur syngas
- Completed acquiring hydrodynamic data for the sorbent at key regions within the fluid-bed reactor system using the existing cold-flow unit (Milestone 4)
- Collected hydrodynamic data with effect of pressure and temperature in the hot-flow unit
- Data collected at a combination of pressure and/or temperature to enable extending the application of the data to commercially relevant operating conditions
- Performed cyclic sorbent sulfur testing in the hot-flow unit under simulated operating conditions to collect data for process modeling and techno-economic assessment

16% Complete 100
Subtask 3.1: Cold-Flow Testing

- Transport reactor absorber
  - Mixing zone-Riser Design
    - 8” mixing zone and 4” riser
- 6” fluidized bed regenerator
- 2” transfer lines
- Line size slide valves
  - Recirculation and transfer
- Two cyclones in series
- Extensively instrumented with dP transmitters
Milestone 4 Complete – Acquisition of Cold-Flow Hydrodynamic Data

- Acquisition of Cold-Flow Hydrodynamic Data

- Mixing zone sorbent density vs Riser sorbent density

- Fractional mixing zone height vs Sorbent holdup

- Riser sorbent flux vs Riser density, lb/ft³

- Regenerator bed density vs Superficial gas velocity
Subtask 3.2 and 3.3: Hot-Flow Testing

- Design similar to the cold-flow unit
- Operating limits of 150 psig and 650°C
- Generated hydrodynamic data at ambient conditions and by varying operating pressure and temperature
- Completed cyclic adsorption-regeneration testing in August 2020
Task 4.0: Fixed-Bed Sorbent Development

- Objective: Develop a fixed-bed sorbent and process for its inherent suitability for small-scale modularized systems
- Proven chemistry of the fluidizable form will be leveraged by using co-precipitation wet cake to optimize the process of making extrudates
  - Received pilot-scale wet cake from Clariant (WDP sorbent licensed supplier) – Milestone 2 complete
  - Optimization parameters of interest are binder material and composition, and calcination temperature
- Physical properties of fresh and used sorbents will be tested for surface area, compositional analysis, XRD, and crush strength
- Parametric testing used to optimize fixed bed process parameters (time sequences, regeneration conditions, purge, etc.)
- Multicycle stability of the optimized fixed-bed sorbent tested for >20 cycles
Steam reforming catalysts crush strengths in the range of 25 to 50 N/mm
Balancing Crush Strength and Porosity

- Crush strength represents mechanical strength against compression
- Porosity improves internal mass transfer diffusion and shrinks the length of MTZ
- Balancing is key to achieving extrudates of optimal performance
- Use of pore formers to strike the desired balance

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<td>Pore volume</td>
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Balancing Pressure Drop and Internal Mass Transfer Diffusion

- Smaller particle size lower mass transfer limitation but increase pressure drop
- Preferred particle size is the smallest that still has a tolerable pressure drop. Common particle size range: 2-4 mm
- Bed length did not impact the MTZ, while increasing bed utilization. Higher bed length increase pressure drop.
- Higher space velocity helped decrease the length of MTZ, while increasing the pressure drop.
Impact of Adsorption Temperature and Pressure

Graphs showing the impact of adsorption temperature and pressure on the normalized H2S concentration as a function of time on stream. The graphs depict data for temperatures of 480°C, 515°C, and 550°C, as well as pressures of 5 barg and 19 barg.
PTSA Process Can Get Complicated

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A: Adsorption  
D: Depressurization  
P: Pressurization  
1H: 1st Heating  
2H: 2nd Heating  
P Re: Rest  
C: Cooling

Cycle Time (h):

0  2  4  6  8  10  12  14  16  18  20  22  24  26  28  30  32  34  36
Adsorption – Regeneration Transition

Graph showing effluent H₂S/SO₂ concentration and process temperature over time.
• Regeneration Exotherm was captured in the scaled-up sorbent testing.
• Results were used to identify the minimum temperature requirement to light off the sorbent regeneration process.
Pressure did not impact the kinetics of sorbent regeneration. Atmospheric regeneration will help save on the energy required for feed gas compression.
Task 5.0 Techno-Economic Analysis

- Objective: Develop and optimize conceptual designs for desulfurization processes based on fluidized-bed and fixed-bed reactors
- Data generated from Tasks 2, 3, and 4 being used to develop and optimize fluidized-bed and fixed-bed processes
- Potential to reduce system cost through standardization, modular production and other advanced manufacturing techniques will be investigated
- TEAs developed in this task are for the overall plant from upstream gasification to syngas conversion
- Sensitivity analyses will be utilized to help optimize the overall system integration and to assess relative benefits of RTI’s WDP
Conclusions

- Proposed project builds on decades of effort invested in the development of RTI’s Warm Syngas Cleanup technology
- Validated excellent performance of sorbent at low-sulfur syngas conditions extending its application to low-sulfur coals (Milestone 3)
- Completed generating ambient condition hydrodynamic data for the development of fluidized-bed regenerator at ambient conditions (Milestone 4)
- Studied the effect of pressure and temperature on sorbent hydrodynamics and recently completed cyclic sorbent sulfur testing in the hot-flow unit under simulated operating conditions
- Successfully used pilot-scale fluidizable sorbent wet cake for the optimization of fixed-bed sorbent and process (Milestone 2)
- Currently finalizing conceptual designs for desulfurization processes based on fluidized-bed and fixed-bed reactors to support TEA
- Investigating commercial interest with varying sources for low sulfur, fixed-bed applications
Acknowledgements

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  - Co-operative agreement number: FE-0031522

- Steven Markovich – Project Manager
Questions?

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