H_2S Resistant Steam Reforming Catalysts for Upgrading Coal Derived Syngas for Coal-to-Liquids Production

Andrew Lucero*, Amit Goyal, August Meng, Jonathan Carroll, Kevin McCabe, and Santosh Gangwal,
Southern Research, Durham, NC, USA *ALucero@southernresearch.org

SOUTHERN RESEARCH
Solving the world's hardest problems.

Project Background

DOE NETL Cooperative Agreement DE-FE0012054

❑ **Southern Research** in cooperation with US Department of Energy-NETL is developing a high concentration H_2S resistant reforming catalyst for increasing syngas yields derived from low rank coal and biomass gasification.

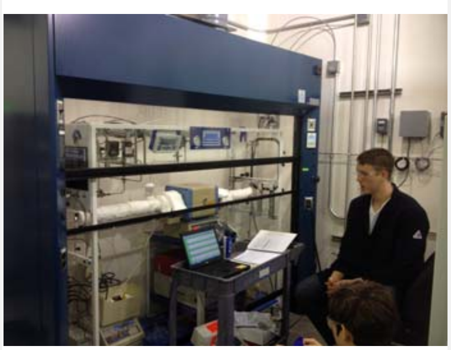
- Conventional low rank coal and biomass gasified syngas streams contain sulfur, residual methane, tars and ammonia which are usually removed via gas clean up processes before Fischer-Tropsch reactor to produce liquid fuels.
- Highly adaptable sulfur resistant catalyst technology for coal and coal biomass syngas upgrading potentially allows lowering the capital costs, GHG emissions (via biomass utilization) and is an easy retrofit to existing gasifiers. It allows US coal industry to further improve process carbon efficiencies.

Project Goals

- ❑ To increase the yield and possibly H_2:CO ratio of a raw low-rank coal syngas by high temperature reforming prior to sulfur removal
- ❑ Develop catalysts for simultaneously reforming of tars, methane, and C_2-C_6 hydrocarbons, and decomposing NH_3 in the presence of H_2S
- ❑ Demonstrate the performance of the catalyst(s) in a lab-scale reactor version of the catalytic reforming process at commercially viable conditions
- ❑ Preliminary techno-economic model that will be used to evaluate the commercial viability of this process relative to the current state-of-the art

Potential Technical Advantages

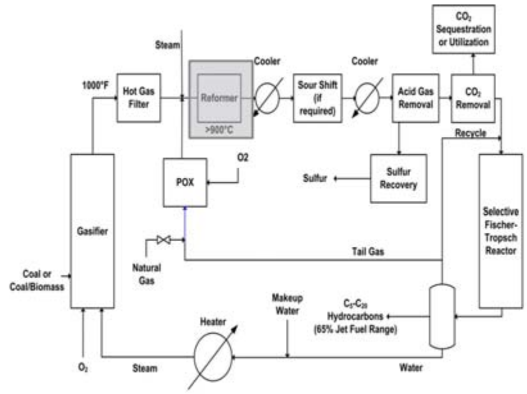
- Tar, methane, light hydrocarbons, NH_3 conversion to additional CO and H_2 in one step
- Reduce or eliminate requirements for a water-gas shift step
- Potential for Fischer-Tropsch (FT) tail gas to provide heat for the reforming and increase syngas yield to FT liquids
- Sulfur tolerant reforming catalyst allows use at any stage of cleanup
- Adaptable to all coal or coal-biomass gasification technologies
- Increasing the energy efficiency of gasification using high-temperature gas clean up



- Lab scale micro-reactor system constructed for tests
- 12 reforming catalysts synthesized, characterized and screened for performance using simulated TRIG and Lurgi gasifier syngas with up to 500 ppm H_2S.
- Three catalysts showed high reforming activity in the presence of H_2S for extended periods of time

Process Flow Diagram and Results

❑ **CTL Process Under Development**



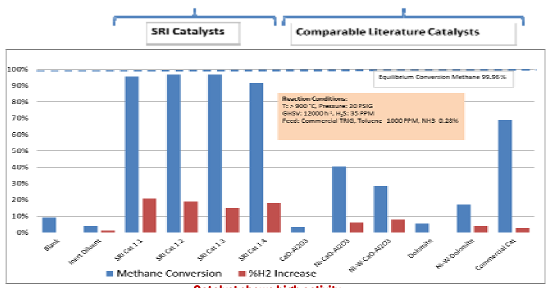
- Transport Reactor Integrated Gasifier (TRIG)
- Steam reformer prior to cooling syngas
- POX on recycled gas or natural gas to generate heat for reformer
- No tar and ammonia cleanup processes needed
- High-activity liquid-selective FT Catalyst that does not produce wax (SR/NETL Project DE-FE0010231)
- Little to no product upgrading

Feed Compositions: Probstein, R. F. and R. E. Hicks (2006)., Driscoll D. (2008).

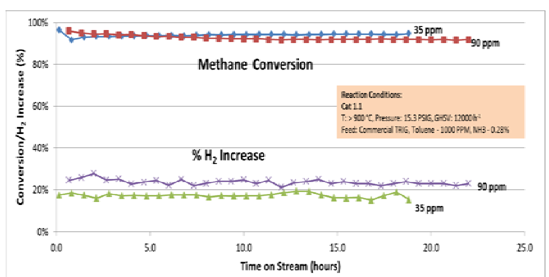
	H_2	CO	CO_2	CH_4	H_2O	H_2S	NH_3	Tar
TRIG - lignite	**29.2%**	**34.3%**	**13.6%**	**2.5%**	**18.9%**	**100-250 ppm**	**.28%**	**.10%**
Lurgi's FBDB - lignite	18.7%	7.5%	15.7%	5.2%	51.6%	.29%	.58%	.41%

❑ **Catalytic Studies Results:**

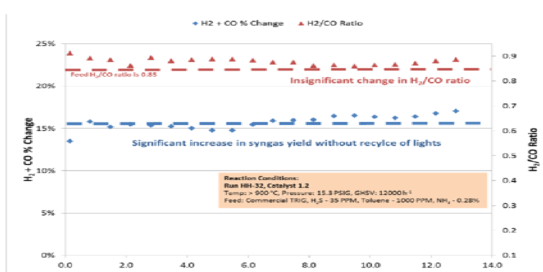
❑ Results obtained over Southern's proprietary catalysts show resilience to H_2S with high activity as compared to five comparable literature/commercial catalysts



Catalyst shows high activity



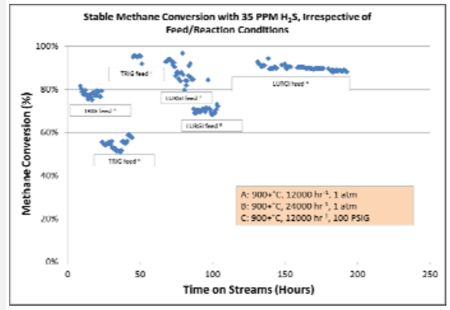
High methane conversions in presence of high H_2S



Approximately ~20 % increase in syngas yields. Insignificant increase in H_2:CO ratio without additional steam.

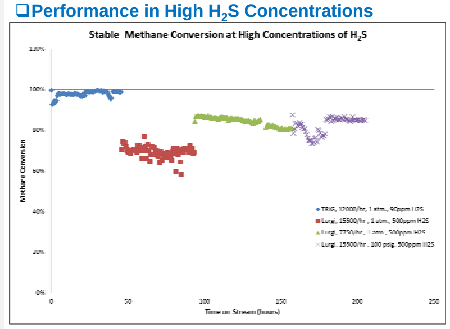
Catalyst Stability and Preliminary Economics

❑ **Catalyst Stability**



- No catalyst deactivation observed for ~ 220 hours on stream under different feeds and reaction conditions.
- Catalyst adaptable for varying steam to methane ratios, H_2S/Tar conc. and system pressure depending on feeds and type of gasifier employed.

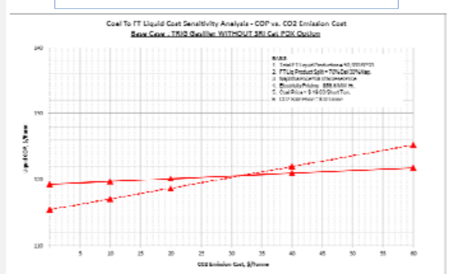
❑ **Performance in High H_2S Concentrations**



- No effect of 90 ppm H_2S on methane conversion
- Reduced conversion in 500 ppm H_2S, but
- Minimal reduction of performance over 200 hours of exposure to high concentration of H_2S

❑ **Preliminary Economics for CTL with Iron catalyst**

Cost of Production for 50,000 BPD plant with CO2 sequestration featuring TRIG Gasifier and Iron FT catalyst	Base case	With POX/ Reformer
Feel Coal (Ton/day)	35,856	26,389
Output liquid products (BPD)	49,996	49,996
Net Power Production (MWe)	354	-47
CAPEX $MM Total Overnight Cost (TOC)	$5,859	$5,625
Cost of Production (Equivalent Petroleum Diesel, $/gal)	$3.41	$3.43



Summary

I. Promising catalyst candidates synthesized and tested at lab scale with 35 to 500 ppm H_2S

II. Catalyst studied showed no significant reduction in activity for ~ 220 hours for 35 ppm, 50 hours for 90 ppm H_2S, and significant tolerance to 500 ppm H_2S

III. Significant increase in syngas yields using raw syngas feed, however no appreciable changes in H_2:CO ratio without additional steam

IV. Preliminary TEA modeling of 50,000 bpd plant indicates greatly improved FT yield for given coal feed rate (less coal needed for given FT output), but near identical costs for FT production due to much less power produced. CO_2 emission costs and power price have large impacts on economics. 50% reduction in carbon emissions per barrel of FT liquids.

Acknowledgements: Darryl Shockley DOE/NETL Project Manager

U.S. DEPARTMENT OF ENERGY

DOE/NETL 2015 Gasification Systems and Coal & Coal-Biomass to Liquids (C&CBTL) Workshop
Morgantown, WV, August 10-11, 2015