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Coal-Derived Warm Syngas Purification and CO_2 Capture-Assisted Methane Production

Final Executive Summary

October 2014

RA Dagle
XS Li
KA Spies
JE Rainbolt
B Braunberger
DL King
R Xing
Y Zhu
L Li

U.S. DEPARTMENT OF ENERGY

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RA Dagle*[1]
XS Li[1]
KA Spies[1]
JE Rainbolt[1]
B Braunberger[2]
DL King[1]
R Xing[1]
Y Zhu[1]
L Li[1]

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Pacific Northwest National Laboratory
Richland, Washington 99352

* Corresponding Author

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[1] Pacific Northwest National Laboratory, Richland, Washington
[2] Western Research Institute, Laramie, Wyoming

Final Executive Summary

Gasifier-derived synthesis gas (syngas) from coal has many applications in the area of catalytic transformation to fuels and chemicals. Raw syngas must be treated to remove a number of impurities that would otherwise poison the synthesis catalysts. Inorganic impurities include alkali salts, chloride, sulfur compounds, heavy metals, ammonia, and various phosphorus-, arsenic-, antimony-, and selenium-containing compounds. Systems comprising multiple sorbent and catalytic beds have been developed for removing impurities from gasified coal using a warm cleanup approach. This approach has the potential to be more economical than currently available acid gas removal approaches and improves upon currently available processes that do not provide the level of impurity removal required for a catalytic synthesis application. Gasification also lends itself much more readily to the capture of carbon dioxide (CO_2), which is important in the regulation and control of greenhouse gas emissions.

A material for carbon dioxide capture was developed for the warm temperature range (250 to 400ºC), and in this study, the material was demonstrated to assist in methane production from purified syngas. Simultaneous CO_2 sorption enhances the carbon monoxide methanation reaction through relaxation of the thermodynamic constraint, thus providing an economic benefit rather than simply being an add-on cost for carbon capture and release. Molten and pre-molten $LiNaKCO_3$ can promote magnesium oxide (MgO) and MgO-based double salts to capture CO_2 with high cycling capacity. Stable cycling CO_2 capacity up to 13 mmol/g was demonstrated. This capture material was specifically developed in this study to operate in the same temperature range and therefore integrate effectively with warm gas cleanup and methane synthesis. By combining syngas methanation, water-gas-shift, and CO_2 sorption in a single reactor, a 99% single pass yield to methane was demonstrated at 10 bar and 330^{o}C when a 20 wt% $Ni/MgAl_2O_4$ catalyst and a molten-phase promoted MgO-based sorbent were used. Under model feed conditions, both the sorbent and catalyst exhibited favorable stability after multiple test cycles.

Warm gas cleanup of inorganics involved three major steps: 1) removal of chloride, 2) removal of sulfur, and 3) removal for a multitude of trace metal contaminants. Sodium carbonate was found to optimally remove chlorides at an operating temperature of 450ºC. For sulfur removal, two regenerable ZnO beds are used for bulk hydrogen sulfide removal at 450ºC (<5 ppm sulfur) and a non-regenerable ZnO bed for H_2S polishing at 300ºC (<40 ppb sulfur). We also found that sulfur from carbonyl sulfide could be adsorbed (to levels below our detection limit of 40 ppb) in the presence of water that leads to no detectable slip of H_2S. Finally, a sorbent material composed of copper and nickel was found to be effective in removing trace metal impurities such as AsH_3 and PH_3 when operating at 300ºC.

Proof-of-concept of the integrated cleanup process was demonstrated with gasifier-generated syngas produced at the Western Research Institute using Wyoming Decker Coal. When operating with a feed rate of approximately 1 standard liter per minute, multiple inorganic contaminant removal sorbents and a tar-reforming bed were able to remove the vast majority of contaminants from the raw syngas. Employing a tar-reforming catalyst was necessary because of the tars generated from the coal gasifier used in this particular study. We envision that, in a real application, a commercial-scale coal gasifier operating at a higher temperature would produce a smaller or negligible amount of tar. Continuous operation of a poison-sensitive copper-based water-gas-shift catalyst located downstream from the cleanup steps was successfully demonstrated.

A preliminary techno-economic analysis confirmed that the warm syngas cleanup process offers potential for significant thermal efficiency compared to the sizable heat loss associated with water quenching and scrubbing in the cold syngas cleanup process. However, areas of improvement are needed for the warm syngas technology; specifically, CO_2 sorbent kinetics need to be improved before commercial implementation would be practical. Relatively high equipment cost required for the integrated synthesis and sorption bed(s) would be alleviated for systems with lower CO_2 capture requirements, such as producing syngas instead of natural gas or hydrogen. Overall, given future material improvements, there is clear potential for economic benefit.

Go to http://www.pnnl.gov/main/publications/external/technical_reports/PNNL-23777.pdf to access the complete report.

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