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Supercritical CO_2 cycles for power production

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Abstract

The Allam Cycle is a Brayton cycle utilizing supercritical CO_2 as working fluid providing high thermodynamic efficiency and integrated CO_2 capture. The Energy & Environmental Research Center, 8 Rivers Capital, LLC, and the North Dakota Industrial Commission Lignite Energy Council are working to develop lignite-based Allam Cycle technology in support of ALLETE, Inc., and Basin Electric Power Cooperative. Specific challenges are gasifier selection, syngas impurities removal, and corrosion . Results from laboratory experiments and pilot-scale testing to support this effort are presented. No insurmountable technology barriers were found for development of a lignite-based Allam cycle technology.

Peer-review under responsibility of the organizing committee of GHGT-13.

Keywords: Allam Cycle; carbon capture; oxy-fired syngas combustor; lignite gasification; syngas impurities

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1. Introduction

The Allam Cycle is any supercritical CO_2 Brayton cycle that is oxy-fuel and direct-fired with energy generated in a high-pressure turbine. Turbine exhaust heat is recuperated back to the combustor via a recycle stream. It is able to utilize heat sources in addition to the turbine exhaust. Turbine inlet temperatures are above 800°C, with optimal temperatures being 1000°–1200°C. Inlet pressures are above 80 bar, with 200–400 bar optimal. The use of supercritical CO_2 as the working fluid allows a very compact design, as well as intrinsically providing a nearly sequestration-ready CO_2 stream. Estimated cycle efficiencies are capable of reaching 47% on a lignite feedstock [1]. In a recent study by Phillips [2], a coal gasification/supercritical CO_2 cycle can offer a 25% to 50% increase in net efficiency over an integrated gasification combined-cycle (IGCC) system with 90% carbon capture and storage. A schematic of the Allam Cycle is shown in Figure 1.

A 50-MWth natural gas-fired Allam Cycle plant is being demonstrated in La Porte, Texas. The plant design mirrors the design of a commercial plant to ensure scalability. The plant includes all components of the Allam Cycle but with oxygen supplied from a pipeline rather than being produced with a dedicated air separation unit (ASU). A larger 300-MWe commercial plant is in the planning stage of development which will further demonstrate the potential of the Allam Cycle. Depending on fuel economics, this plant is expected to be fired on natural gas.

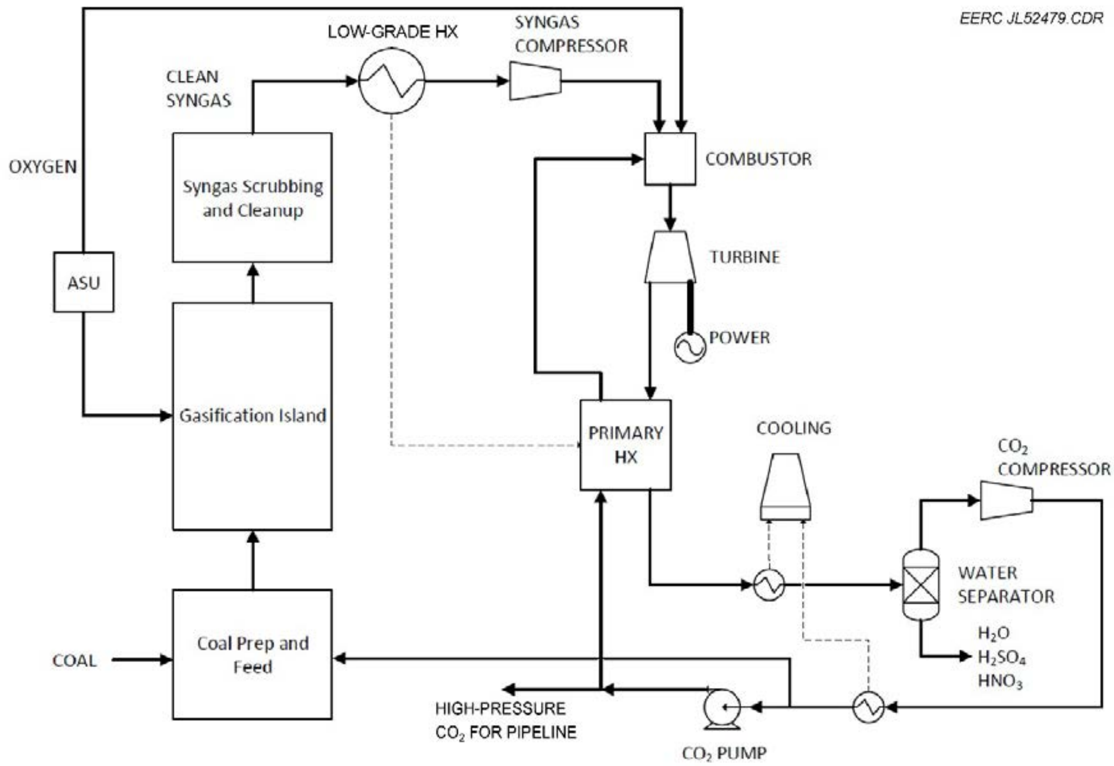

Fig. 1. Schematic of Allam Cycle.

1.1. A lignite-fueled gasification/Allam Cycle plant

Specific challenges for a lignite-fueled gasification/Allam cycle are gasifier selection and integration, corrosion, syngas impurities removal, and design considerations of a high-pressure oxy-fired syngas combustor. The goal is to choose the best technology to gasify North Dakota lignite and integrate gasification with the Allam Cycle to achieve high system efficiency at low cost. A team consisting of the Energy & Environmental Research Center (EERC), 8 Rivers Capital, LLC (8 Rivers), and the North Dakota Industrial Commission (NDIC) Lignite Energy Council (LEC) is working to develop lignite-based Allam Cycle technology in support of an industry team comprising ALLETE, Inc., and Basin Electric Power Cooperative (BEPC). This work is building on the knowledge gained from development of the natural gas-fueled Allam Cycle while addressing challenges to coal-fired applications. The team is addressing potential technology barriers requiring further research and development for lignite-based applications. This ongoing effort will develop knowledge to support the deployment of commercially viable low-carbon power generation technologies for the next generation of coal-fired power plants.

2. Lignite coal properties

Lignite coal possesses certain advantages as fuel feedstock. It is an abundant, low-cost fuel with high reactivity that gasifies readily at relatively low temperatures. The mine sources are generally located in regions of the United States where CO_2 sequestration is a viable option. However, lignite also possesses properties that present challenges to gasifier designs.

North Dakota lignites are characterized by high moisture content, high ash content, and high oxygen content present as oxygen functional groups. Physically, lignites exhibit high friability and do not show plastic properties on heating.

Lignite ash composition is significantly variable from mine to mine, pit to pit within a given mine, and from seam to seam. The ash is characterized by high levels of CaO (12%–32%) and Na_2O (2%–7%). A significant percentage of the calcium and sodium are ions bound as salts of carbolic acids in the organic structure of the coal rather than discrete minerals. This association results in the release of vapor-phase sodium species and a very fine calcium oxide fume under combustion or gasification conditions.

The inorganic composition of the lignite ash, including the amounts of calcium and sodium present, also has an effect on the slag properties. Lignite slags tend to be low-viscosity, with fluid flow at relatively low temperatures compared to slags from bituminous coals. This presents challenges with slag flow and slag layer thickness. Lignite slags also often have their T_{250} (temperature at which the slag viscosity is 250 poise) and T_{cv} (temperature of critical viscosity) temperatures quite close together. This can result in the abrupt freezing of the slag as well as the formation of refractory mineral species by recrystallization that will not easily remelt.

3. Establishment of lignite coal specifications

Currently, five lignite mines are operating in western North Dakota. Lignites from each mine have differing coal and ash properties. The industry team expressed a desire to consider coal from all active mines in the state for the coal-based Allam Cycle. Table 1 provides the average and maximum/minimum analyses values for coal obtained from the mines. These values provide one specification for evaluation of gasifier designs. The range of properties may be challenging for some gasifiers, but the team feels the specification is reasonable.

4. Preliminary gasifier design screening

Gasifier selection is a critical step that will impact all areas of the coal-based Allam Cycle. Gasification is a mature technology, but the particular system must best-fit the feedstock and be compatible with the Allam Cycle. Twenty-two gasification systems were evaluated as to their applicability to be incorporated into the coal-based Allam Cycle using lignite coal as a feedstock. Six criteria were used for ranking the gasifier design technologies:

- Commercial readiness
- Operational history with lignite applicability to lignite
- Cost

- Thermal integration with the Allam Cycle
- System reliability

Nine technologies were selected as most suitable (Table 2). Further downselection will be based on actual costs, commercial guarantees, expected impacts of sodium, and overall system efficiency when integrated with the Allam Cycle.

Table 1. Average lignite properties from North Dakota mines.

	Average	Maximum	Minimum
Proximate analysis, as-received, wt%			
Moisture	37.5	40.0	35.0
Volatile matter	26.0	31.0	21.0
Fixed carbon	28.5	23.5	33.5
Ash	8.0	12.0	6.0
Ultimate analysis, as-received, wt%			
Carbon	42.0	55.0	32.0
Hydrogen	7.0	8.0	6.0
Nitrogen	0.7	0.9	0.5
Sulfur	1.0	1.5	0.5
Oxygen	45.0	50.0	40.0
Ash composition, wt% as oxides			
SiO_2	25.0	35.0	15.0
Al_2O_3	10.0	20.0	5.0
Fe_2O_3	10.0	20.0	5.0
TiO_2	0.5	1.0	0.1
P_2O_5	0.5	1.0	0.1
CaO	22.0	32.0	12.0
MgO	6.0	11.0	1.0
Na_2O	5.0	7.0	2.0
K_2O	1.0	2.0	0.2
SO_3	20.0	30.0	10.0
Higher heating value, as-received, Btu/lb	6600	7200	5800

Table 2. Most suitable gasification technologies.

Name	Gasifier Vendor	Vendor Headquarters	System Type	Feed	Ash	Current Rank
Lurgi	Air Liquide	Germany	Fixed bed	Dry	Nonslagging	1
BGL	Envirotherm	Germany	Fixed bed	Dry	Slagging	2
SE	ECUST/Sinopec	China	Entrained flow	Dry	Slagging	3
TRIG	KBR/Southern Company	USA	Fluid bed	Dry	Nonslagging	4
HTW	ThyssenKrupp Uhde	Germany	Fluid bed	Dry	Nonslagging	5
U-GAS	SES	USA	Fluid bed	Dry	Agglomerated	6
SFG	Siemens	Germany	Entrained flow	Dry	Slagging	7
SCGP	Shell	Netherlands	Entrained flow	Dry	Slagging	8
Prenflo	ThyssenKrupp Uhde	Germany	Entrained flow	Dry	Slagging	9

5. Impurities removal

Syngas exiting the gasifier is cooled to 90°C–260°C prior to filtration of entrained particulate matter. After further cooling, mercury in the syngas stream is removed. Unlike conventional syngas cleanup, reduced non water condensable impurities (H_2S, COS, CS_2, and HCN) are not removed and remain in the syngas. These impurities are burned in the Allam Cycle combustor in an excess of oxygen which converts them to the oxidized form (CO_2, SO_2, SO_3, NO, and NO_2). Removal of these impurities, along with water and excess oxygen from the CO_2 stream, will be performed at the cold end of the heat exchanger at near-ambient temperature and 30-bar pressure. Impurity removal will use the 8 Rivers DeSNO$_x$ process. This process uses only water in a packed spray column to remove sulfur and nitrogen species through oxidation reactions. The resulting products are nitric and sulfuric acid in aqueous solution.

Initial testing of the DeSNO$_x$ process has been completed. The EERC’s high-pressure fluidized-bed gasifier (HPFBG) was operated as any oxy-fired combustor burning lignite coal with a high volume of CO_2 recycle to generate a 95.5% CO_2 and 1% O_2 flue gas containing sulfur and nitrogen impurities at 30-bar pressure. This gas composition and pressure simulated the postcombustion gas stream from the Allam Cycle combustor for introduction into the DeSNO$_x$ column. The test results show that high levels of SO_x removal (>99%) and NO_x removal (~95%) were achieved (Fig. 2). As expected, the pH in the process decreases as aqueous nitric and sulfuric acids form. The EERC is developing methods to maintain the pH at approximately 3 to ensure consistent impurity removal.

6. Metallurgy and corrosion

The combination of nitric and sulfuric acids and water in a CO_2 atmosphere at 30-bar pressure is conducive to aggressive corrosion. A critical step is determining suitable metals for use in the heat exchanger and DeSNO$_x$ spray column. Previous work conducted by 8 Rivers and the National Energy Technology Laboratory (NETL) had determined that carbon steels are not suitable for this application. Other previous work by 8 Rivers indicated that six stainless steel alloys (Alloy 20, AL6X+N, 347 SS, 321 SS, 316L SS, and 304L SS) would potentially be suitable.

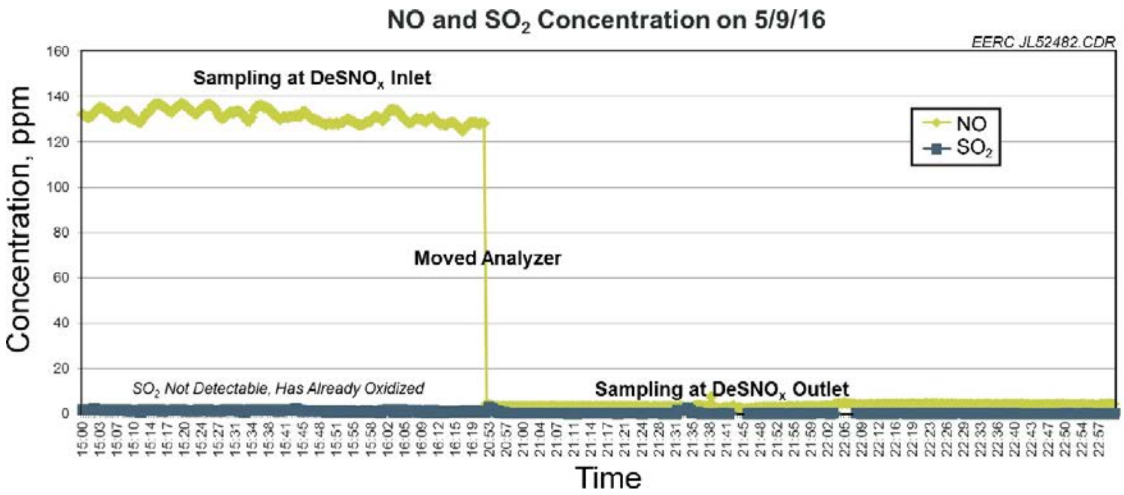

Fig. 2. Levels of SO_x and NO_x removal achieved.

Initial autoclave tests were performed on the alloys at 50°C and 30 bar in an atmosphere consisting of 94.6% CO_2, 1.02% O_2, 2.3% H_2O, 1.02% N_2, 1.06% Ar, 447-ppm SO_2, and 28–30-ppm NO for 120 hours. Coupon preparation, cleaning, and evaluation were performed according to ASTM standard procedure G1. Duplicate coupons were exposed to the gas atmosphere and immersed in water at the bottom of the autoclave. At the end of the tests, the coupons were removed, cleaned, and weighed. The coupons exhibited minimal mass loss, indicating that they held promise as suitable alloys.

A second series of tests at 50° and 90°C under the same atmosphere and pressure was conducted with the alloys for 1024 hours. Coupon samples were removed after 260, 520, and 1024 hours. In this case, besides determining weight change, one coupon of each alloy was examined by scanning electron microscopy (SEM). Results of coupon mass loss testing are shown in Figures 3 and 4. Alloy 20 and Alloy AL6X+N appear to be the most suitable for use. Subsequent testing indicated that pH is a critical factor, with corrosion increasing as pH falls below 4. Although increased corrosion results were seen at low pH, the rates are still acceptable. The use of chemical additives to control pH will add cost to the operation of the $DeSNO_x$ process.

7. Conclusions

Results from design modeling, laboratory experiments, and pilot-scale testing are being used to support the selection of the best technology to integrate gasification with the Allam Cycle. A preliminary screening of gasification technologies compatible with the Allam Cycle and the lignite coal feedstock has identified nine gasifier designs that appear most suitable. Pilot-scale testing of the $DeSNO_x$ process indicates that the technology can achieve high levels of sulfur and nitrogen oxide removal at the planned Allam Cycle postcombustion conditions. The related corrosion testing of potential steel alloys for fabricating the components of the $DeSNO_x$ process equipment identified two alloys with good corrosion resistance. Low pH was found to increase corrosion and may need to be controlled with chemical additives. In summary, no insurmountable technology barriers were found for development of a lignite-based Allam Cycle technology.

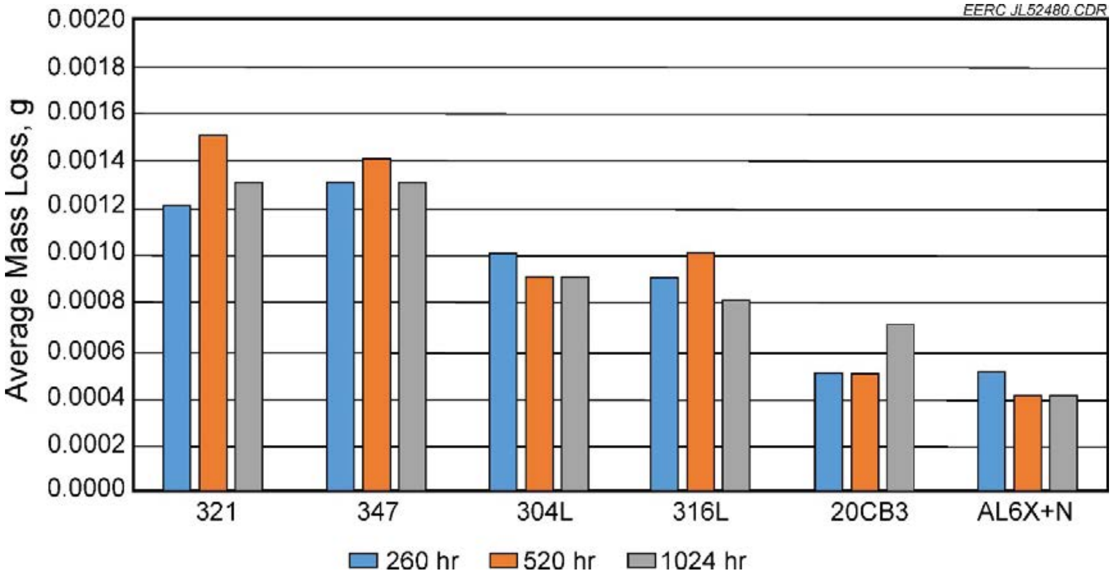

Fig. 3. Coupon mass loss at 50°C.

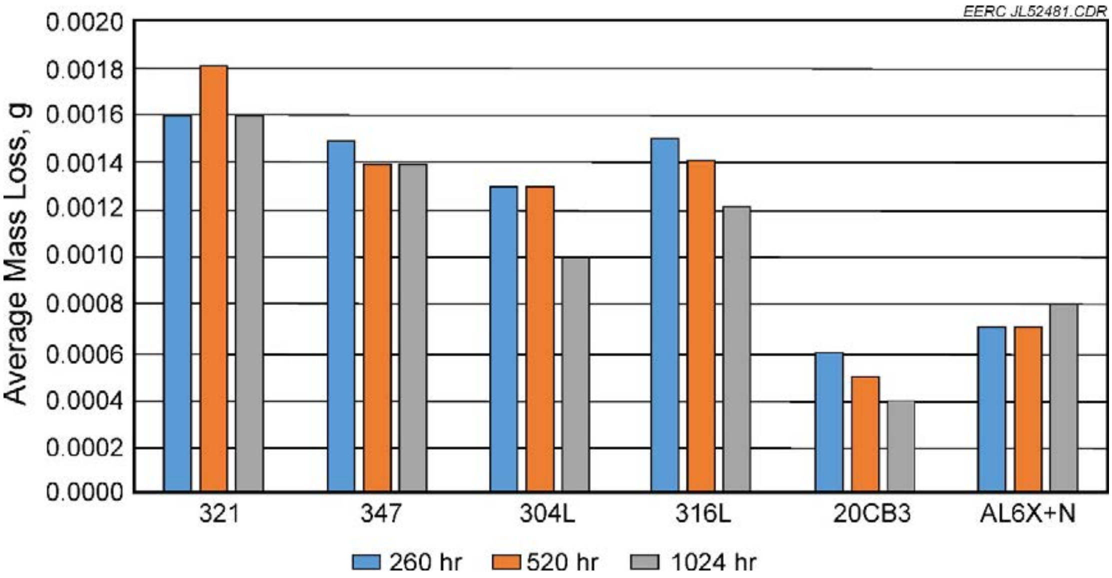

Fig. 4. Coupon mass loss at 90°C.

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