Task 3.17 - Hot-Gas Cleanup

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1.0 INTRODUCTION

Emerging power systems, including pressurized fluidized-bed combustion (PFBC) and integrated gasification combined cycle (IGCC), being demonstrated under the U.S. Department of Energy (DOE) Clean Coal Technology Program, and other technologies at earlier stages in their development will, over time, present opportunities for achieving generating efficiencies of 50% or higher, with stringent control of $\text{SO}_2$, $\text{NO}_x$, and particulate emissions. At their present stage of development and demonstration, these coal-fired technologies offer superior environmental performance for repowering, cogeneration, and greenfield projects at costs comparable to pulverized fuel firing with full stack gas cleaning, but at a considerably higher technical and financial risk. The development of hot-gas cleaning technologies that are less expensive and capable of operating at higher temperatures and pressures will greatly reduce the risks associated with PFBC and IGCC.

Catalytic tar cracking is another issue that advanced power systems are facing at this time. Tars and oils produced during combustion or gasification of coal result in a contaminated gas stream that fouls equipment and makes direct utilization of the stream impractical. Tar production in the gasification of coal is deleterious to the operation of downstream equipment, including fuel cells, gas turbines, hot-gas filters, and pressure-swing adsorption systems, all of which are candidate technologies for use as or in small power generation systems. Cracking of these tars into smaller hydrocarbons is a very important technical issue to be addressed. The oils tend to coat surfaces and enter pores and voids in hot-gas filters and pressure-swing sorbents, causing reduction in efficiencies during hot-gas cleanup. In addition to the problems caused by the oils, the tars, with their high dew points, condense on the surfaces of power generation equipment. Turbine blades can become coated with this condensate, resulting in deviation from acceptable aerodynamics and in the corrosion of metal. Deposits of tars on fuel cell components result in loss of cell efficiency. Tar coatings on gas separation equipment such as membranes, molecular sieves, and filters reduce gas cleanup efficiency. These are some of the operational complications that need to be addressed by this subtask on hot-gas cleanup.

2.0 OBJECTIVES

The programmatic goal in advanced power systems will be to develop advanced methods for gas stream cleanup in combustion and gasification systems, using in situ and back-end technologies. The characteristics of the fuel, its ash, and sorbents will be evaluated to determine their impact on overall performance, including the reduction of gas stream contaminants. Objectives for the work to be performed under this subtask include the following:

- Identifying effective means for hot-gas cleanup and testing in-bed sorbents for accomplishing 99% alkali capture as well as effective capture of sulfur and chlorine during PFBC.
• Developing catalysts and effective operating ranges for removing tar from gasification process streams.

The two activities outlined below correspond to the above-stated objectives for Subtask 3.17.

2.1 Alkali Sorbents

PFBC has been identified as a promising technology for the future. Work will focus on the development of sorbents for in-bed alkali, sulfur, and chlorine capture to reduce or eliminate problems on back-end equipment. Several of the aluminosilicate minerals have the potential to capture alkalies, especially sodium and potassium, under conditions typical of fluid-bed operation (1400° to 1850° F). The alkalies are absorbed on the surface and diffuse into the bulk of the alkali getter. In addition, the nonbridging oxygen atoms released when alkalies modify the aluminosilicate mineral structure are potential sites for sulfur capture. The use of a getter to capture alkali in the bed reduces the need for downstream alkali capture devices. Sulfur capture on the getter also reduces the amount of dolomite needed to meet sulfur emission standards. Chlorine can also be captured by certain types of sorbent. These systems are not without potential problems, however. Modification of the aluminosilicate matrix will lower melting points and could cause sintering and agglomeration problems. This and other potential complications will be addressed.

During FY95, a limited number of alkali sorbent tests were performed. A capture of vapor-phase alkali of 93% was accomplished using kaolin. The final sodium level of 270 ppb is still higher than the 24 ppb recommended by turbine manufactures. The kaolin was also found to significantly reduce agglomeration.

This and other promising sorbents will be tested in the pressurized fluid-bed reactor. A high-sodium North Dakota lignite will be used as the fuel. Parameters to be varied include getter type, feed rate, and size, as well as general operating parameters of the pressurized fluid-bed reactor. Extractive alkali and chlorine sampling will be performed at each condition to quantify the amount of alkali capture. SO₂ will be monitored continuously. The first part of the work will focus on identifying the best sorbent. Work will continue with this sorbent to determine its effectiveness over a wide range of operating conditions.

The fundamental question to be answered by this task is whether in-bed alkali sorbents are technically feasible for capturing alkali in PFBC systems. The impacts of in-bed sorbents on reducing convective pass fouling and blinding of ceramic filter elements may also be investigated. Any related operating problems and improvements in sulfur capture will be noted. If successful, this will benefit industry by reducing the size of and/or the need for back-end alkali removal devices, resulting in substantial capital and operating cost savings.

2.2 Catalytic Tar Cracking

Previous and current work has involved selecting and screening catalysts that are available and relatively inexpensive. Synthetic montmorillonite, a pillared laboratory-prepared clay impregnated with nickel, was initially tested in combination with the feed in the reactor bed and as a separate bed. Conditions needed for the chosen catalyst will be addressed. The effect of temperature, catalyst contact time, and pressure on tar cracking by selected catalysts (e.g., zeolite,
dolomite, or spent petroleum coke cracking catalysts) giving the most highly cracked product will be determined. Successful results from the study will provide an uncomplicated means of tar removal from gas streams with an increase in hydrocarbon content of the usable gas stream.

The work, which will be carried out on the integrated bench-scale gasifier (IBG), will involve evaluating the effect of each of three catalysts on the cracking of tars. In the event that tars escape the catalyst bed, the effect of contact time (bed depth) will be determined. If a reasonable bed depth for cracking all of the tar cannot be found, tandem beds of catalyst and activated char will be tested for their cracking and trapping ability. An effort will be made to regenerate the catalyst, and the spent activated char will be burned under tar-cracking conditions to determine whether the tar can be destroyed by combination combustion-tar cracking.

3.0 ACCOMPLISHMENTS

3.1 Capture of Alkali During PFBC Using In-Bed Sorbents

The work for this task was performed by Michael Mann as his doctoral research for a Ph.D. in Energy Engineering. The outline of his work is presented here along with the conclusions from his work. Details are included in his dissertation which will be presented as a part of the final project report.

3.1.1 Research Outline

PFBC has been identified as a promising technology for the future; however, there are a number of obstacles for maximizing the potential of PFBC. These include removal of 1) fine particulates to eliminate erosion and deposition on turbine blades, 2) alkalies which can lead to corrosion of turbine blades and blinding of ceramic filters, 3) sulfur at very high sorbent utilization efficiencies, 4) halogens that can lead to corrosion, and 5) toxic metals that were specified in the 1990 Clean Air Act Amendments. The primary focus of this research was the removal of alkali from PFBC flue gases to a level specified by turbine manufactures. The target level was less than 24 ppbw. Several of the aluminosilicate minerals have the potential to capture alkalies, especially sodium and potassium, under conditions typical of fluid-bed operation (1400° to 1850° F). The alkalies are absorbed on the surface and diffuse into the bulk of the alkali getter. In addition, the nonbridging oxygen atoms released when alkalies modify the aluminosilicate mineral structure are potential sites for sulfur capture. The use of a getter to capture alkali in the bed reduces the need for downstream alkali capture devices. Other goals of this work were to investigate the potential for simultaneously removing SO2 and Cl from the PFBC gas stream.

Several side benefits were anticipated, and the goal was to demonstrate these during this work. A reduction in the amount of fine particulate was expected when alkali is removed in the bed, since condensation of volatile alkalies is one of the primary mechanisms for the formation of these difficult-to-remove particulates. Improved performance of ceramic filters was expected, since alkalies can lead to bridging, pore plugging, and other problems in ceramic filters. Deposition on the walls of the PFBC and on heat-transfer surfaces can reduce the performance of the PFBC and may be controllable by capture of the alkalies with in-bed sorbents. The propensity of certain fuels
to sinter and/or agglomerate in the fluid bed was also expected to be reduced or eliminated with the introduction of alkali getters.

The work reported here focused primarily on one class of sorbents, sodalites. The goal will be to determine whether sodalites can be used as an in-bed sorbent to simultaneously remove alkali and sulfur. Some of the key reactions that were studied are listed below:

\[
NaCl + 3 (\text{NaAlSiO}_4) \rightarrow Na_4Al_2Si_3O_12\text{Cl} \quad \text{(nepheline)} \quad (\text{sodalite}) \quad [1]
\]

\[
Na_4Al_2Si_3O_12\text{Cl} + 6 \text{SiO}_2 \rightarrow NaCl + 3 (\text{NaAlSi}_3\text{O}_8) \quad (\text{sodalite}) \quad (\text{albite}) \quad [2]
\]

\[
2 (Na_4Al_2Si_3O_12\text{Cl}) + Na_2\text{SO}_4 \rightarrow 2 (\text{NaCl}) + Na_4Al_6Si_6O_{24}(\text{SO}_4) \quad (\text{sodalite}) \quad (\text{nosean}) \quad [3]
\]

\[
Na_8Al_{16}Si_{24}O_{72}(\text{SO}_4) + 12 (\text{SiO}_2) \rightarrow Na_2\text{SO}_4 + 6 (\text{NaAlSi}_3\text{O}_8) \quad (\text{nosean}) \quad (\text{albite}) \quad [4]
\]

\[
2 (Na_4Al_2Si_3O_12\text{Cl}) + \text{SO}_2 + O_2 \rightarrow Na_8Al_{16}Si_{24}O_{72}(\text{SO}_4) + \text{Cl}_2 \quad (\text{sodalite}) \quad (\text{nosean}) \quad [5]
\]

Reactions 1 and 3 are the primary mechanisms for the removal of sodium from the gas stream. In these reactions, nepheline and albite are removing sodium chloride from the gas stream to form sodalite. The fate of the sodalite is dependent upon the other constituents that make up the sorbent/ash bed and the gas stream. For systems high in silica, the potential exists for the silica to react with the sodalite or nosean by Reactions 2 and 4 to release the alkali. Sulfates, on the other hand, will replace the chlorine. In Reaction 3, sodium sulfate reacts to release sodium chloride with no net change in the amount of alkali captured. Provided there is sufficient nepheline, the released sodium chloride could react according to Reaction 1, with the overall result being a capture of both sulfur and chlorine. Reaction 5 shows the exchange of \(\text{SO}_2\) for \(\text{Cl}_2\). For most fuels, the expected concentration of \(\text{SO}_2\) relative to chlorine is high. Therefore, Reaction 5 will likely proceed. The extent of Reactions 2 and 4 will probably depend upon the chemistry of the ash and bed material.

A pressurized thermogravimetric analyzer (PTGA) was used to study the mechanism of alkali capture outlined in Reactions 1 through 5. Further testing was performed on a 3-in.-diameter pressurized fluid-bed reactor. In addition to studying the gettering capability of the sorbent, the impact of the getter on operational performance was evaluated. This evaluation included examining potential agglomeration of bed particles, deposition on heat-transfer surfaces, and the bridging of ceramic candle filters.

**3.1.2 Conclusions and Recommendations**

The work performed as a part of the dissertation consisted of three main efforts: the literature survey, thermogravimetric testing, and bench-scale testing. Conclusions from each of these three efforts are presented. Following the conclusions, recommendations are presented based on the findings of this work.
3.1.2.1 Conclusions from Literature Review

- Electricity generating demands are expected to grow at a rate ranging from 1% to 2% per year in the United States, creating a need for over 200 GW of new generating capacity. PFBC is projected to capture up to 25% of the new market for advanced coal technologies, with much of its market penetration in the area of repowering. Therefore, PFBC is expected to be a major source of new power in the 21st century.

- A number of issues must be resolved for PFBC to capture its projected share of the market. These issues include reducing capital costs and improving reliability and environmental performance. Technical issues related to hot-gas particulate removal, alkali and chlorine control, trace emissions, and the use of advanced cycles must also be resolved for PFBC to reach its full potential.

- The reactions of organically associated mineral matter are of importance in the operating regime of the PFBC. The alkalies, chlorine, and sulfur will vaporize and condense heterogeneously on the surfaces of other ash particles, condense homogeneously to form very fine aerosols, or remain in the vapor phase. These constituents can cause agglomeration and ash deposition, bridging and blinding of hot-gas filters, and corrosion and deposition of turbine blades and, therefore, must be controlled to allow proper operation of the PFBC.

- Measured gas-phase alkali concentrations of 500 to 4000 ppm, depending upon coal type, are high relative to turbine blade specifications of 24 ppb. Therefore, turbine manufacturer specifications for vapor-phase alkali are exceeded even though less than 1% of the total sodium in the fuel is present as vapor. Gas-phase alkali will be higher for those fuels higher in chlorine. The sodium sulfate concentration in the gas phase remains relatively constant because of condensation.

- When using sorbents in the bubbling fluid bed for adsorption of components from the gas phase, the outlet concentration of the controlled gas will vary inversely with the amount of the sorbent utilized. Therefore, very high sorbent feed rates will be required for high removals of alkali from the gas phase. The capture efficiency will vary directly with sorbent particle size for a kinetically limited system and with the square of particle size for diffusion controlled, assuming there is no elutriation of fines from the bed.

- Aluminosilicates have the most potential for adsorbing alkali under PFBC conditions. Bauxite, kaolinite, and emathlite have been demonstrated to effectively remove alkali vapors when used in packed, moving, and fixed beds.

- Reactions leading to the formation of sodalites have the potential for combined alkali and chlorine removal.

- Alkali metals can be measured either on-line producing instantaneous alkali values or off-line using batch sampling techniques. The accuracy of on-line methods is still not reliable enough for use in PFBC. Therefore, batch sampling procedures are recommended even though they only provide average values of alkali metal over a given period of time.
3.1.2.2 Conclusions from TGA Screening Tests

- The PTGA at the EERC could not be equipped to feed a continuous and controlled amount of sodium vapor without extensive modifications. Therefore, testing was performed at atmospheric pressure.

- The atmospheric TGA made a good tool for screening sorbents and determining reaction mechanisms. The TGA allows the impact of gas type, temperature, and alkali concentration to be evaluated and rate data extracted. Samples large enough for analysis by scanning electron microscopy can be generated in the TGA, with these analyses used to help understand the reaction mechanisms.

- Nosean, a sulfur-bearing zeolite, was the favored reaction product when using sorbents for combined alkali, chlorine, and sulfur under the conditions tested. Sodalite, the chlorine-bearing counterpart, would be favored at higher chlorine-to-sulfur ratios and/or higher oxygen partial pressures. Albite reacts with NaCl vapor in an SO₂-bearing gas to capture sodium. The primary mechanism is condensation of Na₂SO₄ on the surface of the albite followed by chemical reaction. The rate of sodium adsorption decreases with decreasing SO₂ concentration in the gas phase because of reductions in the amount of condensed sulfate.

- Albite, quartz, and kaolinite captured sodium by chemical reaction and were kinetically limited. Sodalite and bauxite use physical adsorption as the primary capture method and are diffusion-controlled. After being physically adsorbed, some reaction occurs to permanently bind the alkali.

- The sorbents identified with commercial potential from the TGA screening tests include albite, kaolinite, and bauxite.

3.1.2.3 Conclusions from Bench-Scale Testing

3.1.2.3.1 General Observations from the Use of Alkali Sorbents

- The pressurized fluid-bed reactor (PFBR) at the EERC provides a good tool for determining the effectiveness of sorbents in controlling ash chemistry in the PFBC. The impacts of sorbents on bed agglomeration, ash deposition, ash distribution and chemistry, filter blinding and bridging, vapor-phase alkali, and sulfur and nitrogen oxide emissions can be determined.

- The use of bauxite and kaolinite as in-bed sorbents resulted in a decrease in NOₓ over the base case without sorbent addition. This may be due to a catalytic effect of the sorbent on the NOₓ formation and destruction reactions, similar to those reported for dolomite.

3.1.2.3.2 Impacts of Sorbents on Ash Distribution

- Tests with the Beulah coal, which is indicative of fuels with high organically bound sodium, tended to show bed agglomeration, deposition on heat-transfer surfaces, and
loosely bonded deposits that hung up in the reactor piping. Reduction of the vapor-phase sodium content using bauxite as an in-bed getter eliminated these problems.

- All sorbents increased the mass loading of ash to both the cyclone and the filter vessel. The fine sorbents (−30 mesh) caused a disproportional increase in cyclone ash while the coarse sorbents (−1/8 inch) caused a disproportional increase in filter vessel ash.

- The fine sorbents displayed a higher tendency to form loosely bonded deposits that hung up in the reactor.

3.2.1.3.3 Impacts of Sorbents on Vapor-Phase Alkali Concentration

- The vapor-phase alkali concentration is directly related to the quantity of organically bound alkali in the fuel. The vapor-phase sodium concentrations measured from the Beulah, Belle Ayr, and spiked Belle Ayr were approximately proportional to the initial sodium concentration in the starting fuel.

- Kaolinite and bauxite were effective and albite was not effective at reducing the vapor-phase alkali concentration. Kaolinite and bauxite captured similar amounts of sodium at comparable add rates, indicating both were equally effective at alkali capture.

- At a 10:1 sorbent-to-sodium add rate, kaolinite and bauxite reduced the vapor-phase sodium concentration to between 500 and 700 ppm. At a 30:1 add rate, the resulting sodium concentration was 270 ppm. Therefore, it is unlikely that the turbine specifications of 25 to 125 ppm total alkali can be reached using in-bed sorbents.

- In-bed sorbents have an increased capture efficiency for higher initial alkali concentrations. For example, 90% reduction in sodium from 3600 ppm was realized for tests with the Beulah lignite but only 67% reduction from 1700 using the Belle Ayr coal at the same sorbent add rate.

- The fine sorbents were more effective at reducing vapor-phase sodium concentrations than the coarser sorbents, indicating that the increases in surface area more than offset the shorter bed residence time experienced by the finer sorbents.

3.1.2.3.4 Impacts of Sorbents on Ash Deposition

- For fuels high in organically bound sodium (Beulah lignite for example), sodium calcium sulfates form dense, tenacious deposits. When alkali sorbents are utilized to capture sodium, the amount of deposition is reduced, and the form changes to loosely bonded, lightly sintered deposits that could easily be removed by sootblowing.

- The use of albite as a sorbent resulted in no change in deposition characteristics. When kaolinite was used, some reduction in deposition was noted; however, considerable amounts of fines deposited in the reactor piping. Bauxite effectively eliminated deposition at add rates of 10:1 bauxite-to-sodium and greatly reduced the deposition at lower add rates. This indicates that certain sorbents themselves have a propensity for deposition
regardless of the vapor-phase sodium concentration since the kaolinite and bauxite were equally effective at reducing the vapor-phase sodium concentration.

- Bed agglomeration was apparent when the Beulah lignite was used. Bauxite effectively controlled agglomeration while albite did not. No evaluation for kaolinite was available from this work.

3.1.2.3.5 Impacts of Sorbents on Filter Performance

- The vapor-phase sodium concentration directly impacts bridging of the ceramic filter used for hot-gas particulate removal. Severe filter blinding was noted when the Beulah lignite, with a vapor-phase sodium concentration of 3600 ppm, was used. When using the as-received and sodium-spiked Belle Ayr (900 and 1700 ppm vapor-phase sodium), no blinding occurred. Analyses indicate the blinding is caused by condensation and freezing of $\text{Na}_2\text{SO}_4$ on the surface of the filter, forming a relatively impervious layer that cannot be removed by backpulsing.

- For the Beulah lignite with a baseline vapor-phase alkali concentration of 3600 ppm, the addition of bauxite at a 10:1 sorbent-to-sodium ratio effectively controlled pressure drop in the filter vessel. An add rate of 3:1 was not effective at controlling pressure drop, while a 5:1 add rate of bauxite was only marginally effective.

- For the sodium spiked Belle Ayr subbituminous with a baseline vapor-phase alkali concentration of 1700 ppm, the pressure drop in the filter vessel never exceeded 10 in. $\text{H}_2\text{O}$ for the entire duration of the tests using both the kaolinite and bauxite as sorbents at the 10:1 add rate. The pressure drop without the use of sorbents approached 15 in. $\text{H}_2\text{O}$, indicating that the sorbents were effectively reducing filter pressure drop.

- The size of the sorbent utilized had no apparent effect on filter pressure drop at similar add rates. Bridging was noted after the test with Beulah coal with bauxite at a 10:1 add rate and only a moderate reduction in vapor-phase sodium concentration. Sodium calcium sulfate was the major component of the bridging material. High sorbent add rates may be effective at eliminating bridges by facilitating high vapor-phase sodium removal, thereby reducing the amount available for homogeneous and heterogeneous condensation to form sticky sulfates.

- During the test program, one of the ceramic filters experienced degradation in the form of spalling from the exterior of the filter. While the filter itself did not fail during the test program, it is speculated that over time this spalling would result in a filter failure. The sodium and sulfur appear to be attacking the protective yttrium coating on certain ceramic filters. Yttrium sulfate appears to be the reaction product. The more mobile phases such as sodium, sulfur, and calcium were found impregnated deep within the surface of the candle.

The overall conclusion from this work is that in-bed alkali sorbents can effectively reduce the vapor-phase alkali concentration. This reduction is of a magnitude great enough to control ash deposition and agglomeration and filter blinding but not to a level low enough to meet current...
turbine manufacturer recommendations for vapor-phase alkali. Bauxite was the best sorbent tested based on its ability to control all of the above-mentioned problems. Kaolinite is less effective because of its tendency to form sintered deposits from its fine fraction. Finally, although sodalite and nosean can be formed and result in combined sodium and chlorine or sulfur capture, they do not form at a rate high enough to make them effective getters under PFBC conditions.

3.1.3 Recommendations

Bauxite and kaolinite are both effective in reducing the vapor-phase sodium concentration. The increased loading to the cyclone and filter vessel indicate that they have a limited residence time in the bed. These tests also indicated that the high surface area of finer sorbents enhanced alkali removal. Therefore, alkali capture could be improved by changing the form of the sorbent to keep the high surface area, but increasing the size and physical strength to give the sorbent a longer in-bed residence time. This could be accomplished by pelleting a fine sorbent into pellets of a size approaching the mean size of the bed material. It is recommended that pelleting techniques be examined to determine if they can be utilized for kaolinite and bauxite. If not, other aluminosilicate materials should be researched to find a selection that has a propensity to adsorb alkalies and can form good, strong pellets. Even if these alternative sorbents may not be as effective as bauxite and kaolinite in their raw form, they could prove to be more effective overall, if pelleting can substantially increase their residence time in the bed.

If bauxite is chosen as a sorbent, consideration should be given to capturing the cyclone and filter ash and recycling the material back to the PFBC. This should improve the overall efficiency of both the bauxite and the dolomite. Pelletizing the material prior to reintroducing it to the combustor would help stabilize the recycled ash and increase its residence time. The presence of the dolomite in the ash may improve the pelleting characteristics. This process has been demonstrated for the recycle of fly ash from the circulating FBC of petroleum coke and increased the utilization of the limestone from approximately 35% to over 70%.

For future testing on the PFBR for screening alkali sorbents, consideration should be given to sampling from the outlet of the filter vessel in addition to the top of the reactor. This would provide an indication of how much, if any, alkali is captured by the entrained ash and the ash that builds up on the filters. Results of other work have shown that SO₂ is captured on the filters as the flue gas passes through the filter cake. These measurements would be a better indication of the final vapor-phase concentration that the turbine blades would see. Tests at various filter vessel temperatures could provide information to determine how much cooling of flue gas is required to lower the alkali content from the nominal 500 to 700 ppb measured during this work to the 25 to 125 ppb recommended by turbine manufacturers.

Testing should continue to find effective in-bed sorbents for PFBC. If the PFBC is to realize high coal-to-electricity conversion efficiencies, inexpensive methods of capturing alkali are required. In-bed sorbents offer the capability to accomplish this goal.
3.2 Catalytic Tar Cracking

3.2.1 Experimental

Steam gasification tests were carried out on a high-volatile Illinois bituminous coal (IBC-101) at 750°C and 100 psig in an integrated bench-scale gasifier (IBG) fitted with a catalyst module at the outlet. The module was attached to the outlet of the reactor to take advantage of the excess reactor heat to keep the catalyst at elevated temperature and to crack the tars before they condensed.

3.2.1.1 Integrated Bench-Scale Gasifier

The IBG is a small batch process gasifier, with a charge capacity of nominally 70 g of coal. This unit provides data on the effects of bed fluidization, conversion of feedstock, reaction rate response to temperature, pressure, catalyst and feed gas composition and flow rate, and gaseous products, while providing sufficient quantities of conversion products for subsequent analysis. The top of the reactor was fitted with a catalyst module through which the hot exhaust gas passed before entering the series of two condensers. Although the catalyst module had no heaters of its own, it received heat from the reactor and tended to remain predictably within 50°–100°C of the reactor. A typical catalyst charge to the module was approximately 90–300 g. Gas flowed uninterrupted through the system. Gas exiting the second condenser was collected in gas bags at 12-minute intervals. The gas was analyzed by a refinery gas analyzer. The effect on the tar was determined by measuring the levels of methane and other hydrocarbons in the gas stream and the weight of the tar recovered from the system. In this study, EMcat Elite S-3699 was tested for its tar-cracking effect.

3.2.1.2 Gasification Tests

Four tests were carried out on identical quantities of coal under the same conditions of time, temperature, pressure, fluidization gas (N₂) velocity, and steam injection with approximately 0, 90, 180, and 270 g (module full) of Engelhard EMcat Elite S-3699. This zeolite catalyst was impregnated by the manufacturer with <1% Pt.

Each 60-minute test was carried out on 75 g of feed with gas samples drawn each 12 minutes. Fluidization of the -60-mesh coal was achieved with nitrogen carrier gas flow of approximately 9.4 L/min, and steam was injected at approximately 11 g per minute. Gas–catalyst contact times were 0, 1, 2, and 3 seconds. Solids and tar recoveries were obtained, and gas was collected and analyzed.

3.2.2 Results

Production of heavy tar always accompanies steam gasification of coal. This tar is detrimental to the process for several reasons, including environmental, operational, and product economics. Aerosols that escape into the atmosphere degrade air quality as well as surfaces on which they condense. Condensed droplets result in equipment fouling. This is particularly undesirable in processes, such as cogeneration, which utilize turbines. In addition, tar formation seriously affects the energy/lb of coal available as gaseous fuel. Conversion of this tar to additional gas and, at the same time, removing the fouling problems would impact the economics of the process. Catalytic tar
cracking is one solution to the problem. The search for an inexpensive, efficient catalyst is a necessary part of this solution.

Engelhard EMcat Elite S-3699 was tested for tar cracking of coal tar produced during steam gasification. The effect of this catalyst in cracking heavy tar produced during steam gasification of IBC-101 is demonstrated by the increased total gas production and coincident decreased total heavy tar yield with increasing Pt-zeolite-tar contact time shown in Figure 1.

The effect of cracking on hydrocarbon production from hydrogasification of the tar is shown in Figure 2. As hydrocarbon production increases, hydrogen in the gas stream decreases.

Increased tar–catalyst contact time resulted in increased tar conversion to gas as shown in Figure 3. With the current catalyst module full and the gas flow rates set as above, tar–catalyst contact time was 3 seconds. At those conditions, 80% of the tar was cracked. Hydrogasification occurred using only the hydrogen produced by the gasification reaction.

### 3.2.3 Conclusions

- EMcat Elite S-3699 will crack coal tar.
- Tar–catalyst (EMcat Elite S-3699) contact time of 3 seconds cracked 80% of the tar entrained in the hot-gas stream.
- Tar cracking increased linearly with tar–catalyst contact time for 0–3 seconds.

### 3.2.4 Recommendations

- Determine cracking with the same catalyst at increased contact time.
- Determine the effective life of the catalyst.
- Perform the same suite of tests using dolomite as the cracking catalyst.
Figure 1. Effect of catalyst–tar contact time on tar cracking.

Figure 2. Fuel gas production from gaseous tar versus gaseous tar contact with Pt-zeolite catalyst.
Figure 3. Conversion of gasification coal tar to gas as a function of tar-catalyst contact time.
U.S. DEPARTMENT OF ENERGY
FEDERAL ASSISTANCE MANAGEMENT SUMMARY REPORT

1. Program/Project Identification No. DE-FC21-93MC30097
2. Program/Project Title TASK 3.0 ADVANCED POWER SYSTEMS
3. Reporting Period 10-1-96 through 12-31-96
4. Name and Address Energy & Environmental Research Center
   University of North Dakota
   PO Box 9018, Grand Forks, ND 58202-9018 (701) 777-5000
5. Program Start Date 01-12-93
6. Completion Date 12-31-97

7. FY 96/97 8. Months or Quarters

b. Dollar Scale
   JAN FEB MAR APR MAY JUN JUL AUG SEP OCT NOV DEC

9. Cost
   a. Dollars Expressed In Thousands

10. Cost Chart

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P = Planned  A = Actual

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<tr>
<td>3.12 Small Power Systems Commercialization Plan</td>
<td>P</td>
<td>C</td>
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<td>3.15 Impacts of Low-NOx Combustion Fly Ash and Slagging</td>
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12. Remarks

13. Signature of Recipient and Date

14. Signature of DOE Reviewing Representative and Date
**U.S. DEPARTMENT OF ENERGY**

**FEDERAL ASSISTANCE MANAGEMENT SUMMARY REPORT**

1. Program/Project Identification No.  
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01-12-93

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12-31-97

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<th>Description</th>
<th>Planned Completion Date</th>
<th>Actual Completion Date</th>
<th>Comments</th>
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| Subtask 3.12     | Small Power Systems Commercialization Plan  
Develop commercialization plan | 3-97 |          |          |
| Subtask 3.15     | Impacts of Low-NOx Combustion on Fly Ash and Slagging  
Modification of CEPS for Low-NOx combustion and ash deposition | 3-96 | 7-96 | Completed |
|                   |            |                         | 6-96 | 10-96 | Completed |
|                   |            |                         | 8-96 | 12-96 | Completed |
|                   |            |                         | 3-97 |       | Revised Date |
| Subtask 3.16     | Low-Cost CWF for Entrained Flow Gasification  
Procure samples for vendors | 3-97 |          |          |
|                   |            |                         |          |          | Delayed |
|                   |            |                         |          |          |          |
| Subtask 3.17     | Hot-Gas Cleanup  
Screening of PFBC sorbents | 6-96 | 9-96 |          |
|                   |            |                         | 12-96 | 12-96 |          |
|                   |            |                         | 9-98  |      |          |
|                   |            |                         |          |          |          |
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