

FINAL TECHNICAL REPORT
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Project Title: **METHODS TO EVALUATE AND IMPROVE THE GASIFICATION BEHAVIOR OF ILLINOIS COAL**

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ABSTRACT

Destec Energy owns and operates a pressurized, two-stage, slagging, slurry-fed, entrained flow gasifier at the Wabash River Station in Terre Haute, IN as part of a 262 MW Integrated Gasification Combined Cycle (IGCC) power plant. It gasifies more than 900,000 tons of Indiana coal per year. Prior to this study, the gasification reactivity of the Indiana coal (1.7% S, 10.5% ash, 10,800 BTU/lb) and whether it can be improved upon had not been determined. Destec recently expressed interest in learning more about the gasification behavior of Illinois coals with respect to the conditions of their process. An increase in the reactivity of the char produced in the second stage of the Destec gasifier would increase the overall efficiency of their IGCC process. The overall objective of this project, a cooperative effort between the ISGS, Destec Energy, Dow Chemical, and Clark Atlanta University (CAU) was to characterize the gasification behavior of Illinois coal and to explore the possibility of increasing its reactivity through various treatments such as coal preoxidation and/or addition of a suitable catalyst. Since this commercial application precludes the use of alkali metal catalysts, only calcium and iron were studied. The immediate objective is to provide Destec with sufficient data to justify a large scale test with an Illinois coal (18,000 tons) either as-received or modified, e.g., by catalyst addition.

The gasification reactivities of chars prepared from the coals in the Illinois Basin Coal Sample Program (IBCSP) were determined and compared to that of the Indiana coal used in the Destec process. The Indiana coal was found to have the lowest reactivity of all the chars tested except one made from high ash IBC-104 coal. Two Illinois coals were identified that were considerably more reactive, had less ash, more sulfur, and a higher heating value than the Indiana coal; all distinct advantages. To further increase reactivity, selected coals were preoxidized in air at 200°C prior to gasification tests. In all cases the preoxidized coal was either as reactive or less reactive than the original coal. Calcium or iron was ion exchanged onto selected coals under pH controlled conditions. The Ca- and Fe-catalyzed coal chars prepared in this way were significantly more reactive than those prepared at their natural pH. The use of gypsum (CaSO₄) as a catalyst precursor, instead of calcium acetate, was also examined. Results showed that Ca-catalyzed char prepared using gypsum under pH controlled conditions was significantly more reactive than untreated char. Since the solubility of gypsum is quite low, these results were unexpected. Destec has shown interest in the concept of using gypsum instead of limestone, which is currently added to their feed coal to modify slagging behavior. Limestone has no effect on coal reactivity. Further work is needed to determine the full potential of gypsum as a catalyst precursor in coal gasification processes.

Pages 10 through 25 contain proprietary information.

EXECUTIVE SUMMARY

Coal gasification for integrated combined cycle derived power for utility and other industries is expected to become an essential component for energy production in the next century. IGCC processes that utilize high sulfur coal typically achieve power generation efficiencies in excess of 40%. Illinois Basin coal is a proven feedstock in IGCC processes, however, further research is needed to optimize the gasification behavior of Illinois coals in two-stage entrained flow gasifiers such as the one now in operation at the PSI Wabash River Generating Station in Terre Haute, IN. The Wabash River Coal Gasification Repowering Project is a joint venture between Destec Energy, Inc. (Houston, Texas) and PSI Energy, Inc. (Plainfield, IN). They have designed, developed, constructed, and now operate a commercial IGCC power plant. PSI is responsible for the new power generation facilities and modification of the existing unit, while Destec is primarily responsible for the coal gasification plant. Their process is ideally suited for high sulfur coal, since sulfur is a saleable byproduct. The facility, which began operation in August 1995, gasifies 2,500 tons of Illinois Basin coal per day to produce 262 MW of power. They recently set a record for most continuous hours of operation using bituminous coal.

The ISGS has played a prominent role in the recent commercialization of IGCC technology in the Illinois Basin region. A 400 ton test of Illinois coal, suggested by the ISGS and performed at the Plaquemine facility in 1990, showed for the first time that Illinois coal, a caking coal, could be used effectively in this process. In fact, the performance of Illinois coal surpassed that of the subbituminous coal that was in use at the time. Continued use of Illinois coal at this facility, however, was not possible since the sulfur recovery unit at this plant was designed and built for low sulfur coal. The new facility in Terre Haute is the first of its kind to utilize high sulfur Illinois Basin coal to produce power by IGCC. Research is needed to realize the full potential of Illinois coal in these two-stage processes. The results of such research could lead to expansion and creation of new markets for Illinois coal.

A window of opportunity exists to encourage further use of IGCC technology in the Illinois Basin region. The proposed research seeks to gain a better understanding of the gasification behavior of Illinois coal in IGCC processes that could utilize high sulfur Illinois coal. There is a lack of information on how Illinois Basin coals will perform in these systems. This project will examine in a systematic way the gasification reactivity of Illinois coals obtained from active mines throughout the state. The generated data should be of use to scientists and engineers considering the use of Illinois coal in commercial coal gasification systems.

In the majority of IGCC gasification processes (e.g., Texaco, Shell), coal is gasified using only one stage at very high temperatures (1400°C) and in pure oxygen. In such a process, the coal delivered to the gasifier is completely converted to gaseous products within seconds; therefore, the intrinsic reactivity of the coal is not as important as it would be in, say, a two-stage process (e.g., Destec), where gasification occurs at a much lower temperature (900-1100°C). The second stage is used to recover most of the heat from the first stage by gasifying additional coal. Since complete char burnout is never achieved in these systems, the reactivity of the coal fed into the second stage is an important process consideration. When the partially reacted char leftover from the second stage is fed back into the first stage, it lowers the overall efficiency of the process since high ash char now replaces some of the low ash feed coal.

The recent development of IGCC technology that utilize a two stage process to gasify coal provides an opportunity for coal researchers to optimize the reactivity of the coal that is added to the second stage of the gasifier. Typically, twenty percent of the feed coal used in the Destec process is added in this stage. However, this feed coal, present in a coal/water mixture (60% coal/40% H₂O), is only partially converted to CO and H₂ in the reducing atmosphere (25% CO, 35% H₂, 30% CO₂) at the

relatively low temperature of 1000°C. The leftover char, which contains anywhere from 30-80% mineral matter, is fed back into the first stage and gasified in pure oxygen at 1400°C. Coals that produce the most reactive chars, i.e., those that achieve the highest level of conversion in the second stage, would improve overall operating performance. Thus, coals with optimal gasification reactivity need to be identified for use in the Wabash River IGCC plant. The coal and resultant char needs to be made more reactive so that higher levels of conversion can be achieved. Proven methods for improving the gasification reactivity of coal include adding a catalyst, e.g., calcium, to the coal. Preoxidation of coal may also increase its gasification reactivity. The results of a recent study indicated that the combustion performance of naturally weathered (oxidized) coals was significantly better than that of deep mined (unoxidized) coals. The pretreatment of coal with oxygen is thought to promote the cross linking reactions between aromatic units in the coal structure preventing their rearrangement during pyrolysis (melting) and increasing the surface area of the resultant char. An increase in available surface area for reaction should increase the gasification reactivity of the char. It remains to be determined what effect preoxidation will have on gasification behavior of Illinois coal under entrained flow conditions. In addition to a possible increase in reactivity, tar formation, which is detrimental to the performance of the Destec process, may be suppressed by preoxidation as well as by the addition of calcium to the coal.

This second year project, a joint effort between the ISGS, Dow Chemical, Destec, and Clark Atlanta University, consisted of six tasks. In Task 1, chars will be prepared from preoxidized coals, catalyzed coals and the Destec feed coal. In Task 2, the gasification reactivity of prepared coals and chars will be determined by isothermal and non-isothermal thermogravimetric analyses. In Task 3, the Combustion Laboratory at PSU will perform gasification tests in a drop tube furnace to simulate the conditions in the second stage of the Destec gasifier. Six of the coal samples prepared in Task 1 will be tested at 1100°C in a reducing atmosphere using a residence time of 3-5 seconds. In Task 4, physical, chemical, and morphological studies will be performed on coal and char samples prepared in Task 1-3 to gain additional insight into the gasification behavior of Illinois coal. Tests to be performed include: surface area, active surface area, pore size distribution, scanning electron microscopy, ultimate/proximate analyses, transient kinetics and temperature programmed desorption. In Task 5, the reactivity data will be evaluated to determine which coals are most reactive. The reactivity of Illinois coal will be compared to that of the Indiana coal currently used by Destec. We will determine which Illinois coal displays optimum gasification behavior and work towards commercial scale testing of that coal. In Task 6, technical and management progress reports will be prepared and submitted to the ICCI.

An analyses of thirty four coals obtained from active mines throughout Illinois showed that several have lower ash content, higher sulfur content and heating value than the Indiana coal presently used by Destec. The gasification reactivities of selected Illinois coals were measured by thermogravimetric analysis and compared to that of the Indiana coal now used in the Destec process. The Indiana coal char had the lowest reactivity of all the chars tested except one made from high ash IBC-104 coal. An Illinois coal having considerably less ash (6.00%), more sulfur (3.68% S) and a higher heating value (12,271 BTU/lb) was about four times more reactive than the Indiana coal. The effects of catalyst addition and preoxidation on gasification reactivity were also examined. Results showed that coal preoxidation has minimal effect on gasification reactivity. The effect of pH (acidic, neutral and alkaline) on ion-exchanging catalysts (calcium and iron) onto Illinois and Indiana coal was also studied. Alkaline pH was found to be most effective. Three- to five-fold increases in reactivities as a function of pH (2.2 to 10) were observed for Ca- and Fe-loaded Illinois coals. However, for some reason, there was little or no effect of pH on reactivity on the Ca- and Fe-loaded Indiana coal. Although coal preoxidation was not an effective means to increase char reactivity, preoxidation of the coal prior to catalyst addition enhanced the reactivity of Ca-catalyzed coal by providing additional ion exchange sites. Destec is also interested in suppressing unwanted tar formation in the second stage of their gasifier. Work was performed to

examine whether coal preoxidation and/or catalyst addition can be used to reduce tar formation. Results showed that preoxidation and/or calcium addition does suppress the release of volatile matter during pyrolysis.

The possibility of using gypsum (CaSO_4), a coal combustion by-product, instead of calcium acetate as a catalyst precursor was also studied. Reactivities of gypsum-catalyzed chars were significantly higher than those of uncatalyzed chars, but lower than those prepared using calcium acetate. The catalytic effect of gypsum was rather unexpected given that gypsum has a relatively low solubility (2 g/L) compared to calcium acetate (80 g/L). The shuttling of calcium from gypsum to coal occurs in such dilute solutions given the proper amount of time. The use of gypsum for preparation of Ca-catalyzed Illinois coal is commercially attractive for several reasons: 1) its low cost compared to other calcium additives, 2) provides new use for coal combustion by-product, 3) could increase recovery of sulfur, a valuable by-product of the Destec process, 4) suppress tar formation, 5) calcium carbonate formed may reduce CO_2 emissions from the gasifier. At a recent meeting held in Champaign, IL, Destec officials expressed interest in the possibility of adding gypsum instead of limestone to their coal water slurry to modify slagging behavior as well as increase coal reactivity. It remains to be determined whether gypsum is a commercially viable catalyst precursor for use in the Destec process.

Further work is needed to modify and test Illinois coals for possible use in the Destec two-stage gasifier. Binary catalyst systems, which have shown considerable promise in lower temperature gasification systems, such as calcium and iron, may provide superior performance compared to equivalent loadings of a single catalyst. Larger scale tests need to be performed using pound quantity samples of optimized Illinois coal and the Indiana coal under process conditions that simulate those used in the Destec gasifier. Process simulations also need to be performed to determine effects of optimized coal on overall process efficiency. ISGS and Destec will continue to work towards commercial scale testing of the Illinois coal that perform best in both process simulation and reactivity studies.

The remainder of this report contains proprietary information and is not available for distribution except to the sponsor(s) of this project.