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 and PSI Energy own and operate a pressurized, two-stage, slagging, slurry-fed, entrained flow gasifier at the Wabash River Station in Terre Haute, IN as part of their 262 MW Integrated Combined Cycle Gasification (IGCC) power plant. It gasifies more than 900,000 tons of Indiana coal per year. To date, the gasification reactivity of this coal (1.7% S, 10.5% ash, 10,800 BTU/lb) and whether it can be improved upon has not been determined. Destec recently expressed interest in learning more about the gasification behavior of Illinois Basin 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 process.

The overall objective of this project, a cooperative effort between the ISGS, Destec Energy and Dow Chemical 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. An important goal was to establish an experimental method to better predict gasification behavior of coals considered for use in the Destec process. The ultimate objective of the project 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.

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 determined and compared to that of the Indiana coal and to nine coals obtained from the Illinois Basin Coal Sample Program (IBCSP). Chars were produced from these coals under identical pyrolysis conditions and their gasification reactivity in 1 atm CO_2 at 850°C determined. The Indiana coal char had the lowest reactivity of all the chars tested except the 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 two times more reactive than the Indiana coal. Another Illinois coal (8.72% ash, 4.14% S, 11,022 BTU/lb) was nearly an order of magnitude more reactive than the Indiana coal. The reason for the exceptional reactivity of this coal and the possibility of utilizing it (or a similar type of Illinois coal) in the Destec process remains to be determined. The effects of catalyst addition (Ca, K, Cu) and preoxidation on gasification reactivity were also examined. Adding 2% Ca or K to IBC-101 coal increased its reactivity by more than a factor of 3 and 6, respectively. Preliminary results suggest that preoxidation has minimal effect on gasification reactivity. Nonetheless, it appears that several high quality Illinois coals need no modification to be significantly more reactive than the Indiana coal.

Pages 11 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. Destec and Dow Chemical gasify the same amount of western coal at their IGCC plant in Plaquemine, LA to produce 161 MW of power.

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 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% H_2O), is only partially converted to CO and H_2 in the reducing atmosphere (25% CO, 35% H_2, 30% CO_2) 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.

The overall objective of this project is to evaluate the gasification behavior of Illinois Basin coal. The possibility of increasing the gasification reactivity of Illinois coal through various treatments such as coal preoxidation and/or addition of a suitable catalyst will also be explored. The project, a cooperative effort between the ISGS, Dow Chemical and Destec Energy, consists of six tasks. In Task 1, coals will be obtained from the IBCSP and from mines throughout the state of Illinois. In addition, Destec will provide the feed coal presently used in their two-stage gasifier in Terre Haute, IN. In Task 2, chars will be prepared from selected coals under nitrogen atmosphere at temperatures between 800 and 1050°C and with heating rates up to 100°C/min. Chars will also be prepared under a reducing atmosphere (e.g., 20% H_2O, 50% CO_2 and 30% CO) at higher pressures (1-20 atm) to simulate the conditions used in the second stage of the gasifier. To increase reactivity of the resultant char, selected coals will be preoxidized in air or impregnated with a catalyst, e.g., calcium or potassium. In Task 3, the gasification reactivity of chars in 1 atm CO_2 at temperatures between 800 and 1050°C will be determined using a thermogravimetric analyzer (TGA). The reactivity (rate versus conversion) profiles will be calculated from the TGA data. A high pressure TGA will be used to measure the gasification reactivity of chars in reducing atmospheres at pressures between 1 and 20 atm and at temperatures between 800 and 1000°C. Reactivity profiles of catalyzed and preoxidized coals will be compared to those of their untreated counterparts to assess the effectiveness of these treatments. In Task 4, surface area, pore size distribution, free swelling index, surface morphology, proximate and ultimate analyses, and heating value of selected coals, modified coals, and prepared chars will be evaluated to gain further insight into the gasification behavior of Illinois coal. In Task 5, gasification data will be evaluated and comparisons made between reactivities of Illinois coals and Destec feed coals. The known order of reactivity for Destec feed coals will be compared with experimental results to assess the effectiveness of the method used to determine gasification reactivity. Destec will perform process simulations on selected coals based on compositional analyses to predict gasification behavior in their process. The performance of chars as determined by TGA experiments will be compared to that predicted by these process simulations. In Task 6, technical and management progress reports will be

prepared and submitted to the ICCI.

The gasification reactivities of chars prepared from nine of the twelve coals in the IBCSP were determined in 1 atm CO_2 at 850-940°C by isothermal thermogravimetric analysis. Chars were prepared in a tube furnace under identical pyrolysis conditions (N_2, 30°C/min, 900°C, 0.5 h) prior to these gasification tests. The activation energy for IBC-101 char gasified in 1 atm CO_2 was about 60 kcal/mole, indicating a chemically controlled reaction regime. An analyses of the reactivity profiles for all nine chars revealed important similarities as well as notable differences in gasification reactivity. The reactivities of IBC-103, IBC-105, IBC-106 and IBC-108 were comparable over the entire conversion range, while IBC-101, IBC-107 and IBC-109 were more reactive. The high ash IBC-104 char was the least reactive. A char made from IBC-102 coal was by far the most reactive. Its reactivity averaged more than five times that of the second most reactive char (IBC-107) over the entire conversion range. Its activation energy (30-47 kcal/mol over the 5-80% conversion range) was relatively low compared to the IBC-101 char. This could have been due to the presence of an inherent catalyst.

An in depth analysis of the key properties of other coals from both Illinois and Indiana was performed. The % ash, % sulfur and heating value of some of the more promising coals in these two states showed that several Illinois coals had significantly better properties than the Indiana coal presently being gasified at Terre Haute. An immediate goal of this project is to provide Destec, Dow Chemical and PSI with sufficient data to allow for a large scale test with Illinois coal, either as received or modified in some way, e.g., by preoxidation. A sample of Indiana coal used by Destec was obtained. The gasification reactivity of the char made from this coal was measured and compared to those made from Illinois coals. The Indiana coal char was the least reactive except for the one made from high ash IBC-104 coal. In fact, two chars made from Illinois coal, having more than twice the amount of sulfur and significantly less ash, were more than twice as reactive as the Indiana coal char.

The effects of preoxidation and addition of a catalyst to the coal was also studied. The reactivity of chars made from several preoxidized Illinois coals and the Indiana coal was either slightly less or similar to the reactivity of the respective as-received coals. Further work will be needed to optimize preoxidation conditions. Calcium or potassium was added to IBC-101 coal (2 weight percent) by an ion exchange method. Calcium and potassium increased reactivity of IBC-101 char by a factor of three and six, respectively. Potassium was a more effective catalyst since it maintains higher dispersion during gasification. Another method of measuring gasification reactivity that involved rapid heating (100°C) of the coal sample in a reducing atmosphere (80% CO_2, 20% H_2O, 1 atm) was used to compare the reactivity of several Illinois coals to that of the Indiana coal. The results from nonisothermal tests, for the most part, confirmed those obtained from isothermal tests. It was interesting that calcium appeared to be a more effective catalyst than potassium during the nonisothermal experiments.

During the next project year, we will continue to obtain, modify and test Illinois coals for possible use in the Destec IGCC process in Terre Haute. Several large scale gasification tests will be performed using pound quantities of optimized Illinois coal and the Indiana coal in an entrained flow reactor under process conditions that simulate those used in the Destec process. We will also obtain new insight into the gasification reactivity of Illinois coal. The reason why some Illinois coals are more reactive than others will be determined. Transient kinetics will be used to measure reactive surface areas of selected chars. In addition, Destec will conduct process simulations on Illinois coals that appear to be good candidates for use in their process. The ISGS and Destec will work towards commercial scale testing of the Illinois coal that performs best in both the process simulations and reactivity tests.

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