

## CHANGING MARKETS AND NEEDS LEAD THE DOE TO REFOCUS AND EXPAND THE INTEGRATED GASIFICATION COMBINED CYCLE TECHNOLOGIES PROGRAM

**Gary J. Stiegel**

U. S. DOE, Federal Energy Technology Center  
P. O. Box 10940, Pittsburgh, PA 15236  
Tel: 412-892-4499  
Fax: 412-892-4822  
E-Mail: stiegel@fetc.doe.gov

**Russell C. Maxwell**

Burns and Roe Services Corporation  
P. O. Box 18288, Pittsburgh, PA 15236  
Tel: 412-892-6247  
Fax: 412-892-4604  
E-Mail: maxwell@fetc.doe.gov

**Keywords:** Integrated Gasification Combined Cycle (IGCC); Gasification; Federal Energy Technology Center (FETC)

### ABSTRACT

Changing market conditions, brought about by utility deregulation and increased environmental regulations, have encouraged the Department of Energy/Federal Energy Technology Center (DOE/FETC) to restructure its Integrated Gasification Combined Cycle (IGCC) program. The program emphasis, which had focused on baseload electricity production from coal, is now expanded to more broadly address the production of a suite of energy and chemical products. The near-term market barrier for baseload power applications for conventional IGCC systems has combined with increasing opportunities to process a range of low- and negative-value opportunity feedstocks to provide incentives for the refocused and expanded IGCC program. The new program is developing a broader range of technology options that will increase the versatility and the technology base for commercialization of gasification-based technologies. This new strategy supports gasification in niche markets where, due to its ability to coproduce a wide variety of commodity and premium products to meet market requirements, it is an attractive alternative. By obtaining operating experience in industrial coproduction applications today, gasification system modules can be refined and improved leading to commercial guarantees and acceptance of gasification technology as a cost-effective technology for baseload power generation and coproduction as these markets begin to open.

### INTRODUCTION

Integrated Gasification Combined Cycle (IGCC) combines gasification with gas cleaning, synthesis gas conversion, and turbine power technologies to produce clean and affordable energy. The combination of combustion turbine and steam turbine is highly efficient in generating electricity. The synthesis gas can be converted to fuels for clean efficient fuel cell generation of power and conversion to high quality liquid fuels. Different variations of the combinations can offer to industry the capability to use low-cost and readily available carbonaceous energy resources and wastes in highly efficient energy conversion options. These options can be selected to meet any of a whole host of market applications as may be suitable for the particular business opportunity. Compared with today's commercial and advanced technologies, IGCC is one of the most efficient and environmentally friendly technologies for the production of low-cost electricity and synthesis gas and can be readily adapted for concentrating and sequestering CO<sub>2</sub>. IGCC is the only advanced power generation technology that is capable of coproducing a wide variety of commodity and premium products to meet future market requirements. Through specific selections of the gasification-based technologies, an IGCC configuration can be built to convert virtually any carbon-based feedstock into such varied products as electric power, steam, hydrogen, high-value liquid fuels, and value-added chemicals.

The basic IGCC process for the production of electricity (see Figure 1) initially converts the carbonaceous feedstock in a gasifier into a synthesis gas, a mixture of carbon monoxide and hydrogen. The synthesis gas is cleaned of particulates, sulfur, and other contaminants and is then combusted in a high efficiency gas turbine/generator. The heat from the turbine exhaust gas is extracted to produce steam to drive a steam turbine/generator. The Brayton cycle gas turbine operating in conjunction with the traditional Rankine cycle steam turbine make up this combined cycle. Gasifier technology and combined cycle integrated in this way offers high system efficiencies and ultra-low pollution levels, ultimately reaching efficiencies of 60%, near-zero pollution, and closing the carbon cycle.

In addition to steam and power, the clean synthesis gas can be catalytically converted into hydrogen, environmentally superior transportation fuels, and a variety of chemicals in the coproduction mode. The high quality steam can also be exported for applications other than the production of electricity.

## **WHY SHOULD INDUSTRY BE INTERESTED?**

IGCC has inherent characteristics which will enable major energy industries -- electric power generation, petroleum refineries, chemicals, fuels, and energy users -- to remold their technology and business structure to meet future market needs and take advantage of new opportunities. Deregulation, restructuring, and new types of cost competition are emerging with increased environmental pressures. As a result, the boundaries of these industries and the business structures will be changing significantly. The inevitable result will be opportunities for lower cost, more efficient, and less polluting energy conversion technologies that complement and contribute to the structural changes in both the technology base and business interests of the major energy industries. The unique advantages of IGCC systems have created a significant market for gasification technologies in industrial market applications. Gasification is the only technology that offers both upstream (feedstock flexibility) and downstream (product flexibility) advantages.

Worldwide energy consumption is expected to grow 75 percent between 1995 and 2020, according to the Energy Information Administration (International Energy Outlook 1998). Almost half of the world's future increase (or increment) in energy demand will occur in developing Asia. China alone expects to more than double its current electric generating capacity by 2015. This nation of 1.8 billion people will be considering new technology as a way to reduce environmental and health challenges from increasing energy consumption while, at the same time, using its abundant coal resources. The United States and the rest of the world will also increase its energy consumption and will confront similar energy and environmental challenges.

## **WHERE IS IGCC TODAY?**

### **Gasification Worldwide**

The stage is set for IGCC to play a major role in the domestic and global energy market. There are over 350 gasification units operating worldwide, producing the equivalent of about 20,000 MW. More than 300 of the units are producing synthesis gas ( $H_2$  and CO) rather than power. The largest concentration of gasifiers is at SASOL in South Africa with about 100 fixed-bed gasifiers. China contains the next largest inventory, licensing more than 20 gasifiers and there are 14 gasifiers operating in North Dakota at the Dakota Gasification plant.

In addition to traditional coal utility IGCC applications, gasification technologies have been used in the conversion of coke, residual-oil, and biomass to power, steam, and chemicals and new facilities are being installed for additional applications. In fact, residual oil and coke account for 50 percent of the feed to gasifiers worldwide. Coal accounts for 42 percent of gasifier feedstock, and natural gas fuels 8 percent of all gasification. With the emphasis on reducing fuel costs, waste disposal costs and CO<sub>2</sub> emissions, a number of small projects will be using biomass as the gasifier feed and are either already operating or are near completion.

There are eight IGCC plants that are in construction or are operating in the petroleum refining industry both domestically and internationally. In these applications, the refinery residues are converted to synthesis gas to fuel a combined cycle and co-produce hydrogen for use in upgrading transportation fuel quality. There has been a great deal of activity in Europe, particularly in Italy where at least four projects are moving ahead that could add 1,500 MW to the Italian power grid before the year 2000. In the U.S., Texaco is operating a 35 MW IGCC at its El Dorado Plant in Kansas. The plant is proving that small-scale gasification combined cycle plants are economical and can convert hazardous waste streams into products. Two additional projects that integrate gasification with refining (the Motiva Refinery in Delaware and the Exxon Baytown Refinery in Texas) have awarded architectural and engineering contracts for design and construction.

### **Competition within Energy Markets**

During the coming years, competition between the types of power systems and fuel resources will continue and as long as natural gas remains readily available and relatively inexpensive, natural gas-based power systems are likely to be the technology of choice. As natural gas becomes more expensive, lower cost energy resource options such as coal and alternative fuels will increasingly become the preferred choice and gasification the best technology to use these resources in efficient IGCC and syngas conversion technologies.

The capital cost for a natural gas-fired combined cycle plant is about one-half the cost of an IGCC plant that gasifies coal. IGCC is capital intensive; it needs economies of scale and fuel cost advantages to be an attractive investment option. However, IGCC costs can be improved by integrating processing steps and energy uses in a synergistic way with industrial applications. For example, gasifiers can operate on low-cost opportunity feedstocks, can be used to convert hazardous waste into useful products, reduce or eliminate

waste disposal costs, and can coproduce power, steam, and high-value products for use within the host plant or for export. Fluidized-bed combustors compete with IGCC in smaller cogeneration markets due to their ability to handle a wide range of feedstocks; however, IGCC has the added advantage of product flexibility, which can make it a more economical option for certain industrial applications.

### Achievements

The key to commercializing technology is to demonstrate, on a commercial scale, its technical, economic, and environmental performance. DOE's Clean Coal Technology Program, a cost-shared effort with private industry, continues to be a cost effective and successful approach for moving technologies from bench scale to the marketplace. Within the structure of this program, there are three IGCC base-load power production projects and a gasification products conversion project that are relevant demonstrations of the level of commercial readiness of gasification-based technologies. These projects are individually and collectively evidencing the maturity of this technology base. The projects are:

- Wabash River Coal Gasification Repowering Project
- Tampa Electric Company IGCC Project
- Piñon Pine IGCC Power Project
- Liquid Phase Methanol (LPMEOH) Demonstration Project

### IGCC PROGRAM

To meet energy market demands and to break the barriers to global commercial acceptance of gasification-based technologies, the IGCC Program strategy emphasizes increased efficiencies, cost reduction, feedstock and product flexibility, and near-zero emissions of pollutants and CO<sub>2</sub>. As a result of the development and demonstration projects funded by the DOE's IGCC program and the CCT program achievements mentioned in the projects above, significant progress has been made to reach the capability shown at the left margin of Figure 2, namely about 40 percent efficiency and \$1,200 total plant cost per KW. It is anticipated that with the continued development of oxygen blown systems, hot gas cleaning, membranes, and advanced gasifier systems that further improvements in efficiency and reductions in cost will likely be achieved as shown in Figure 2. An overall pictorial of the FETC IGCC Product Team's view of IGCC R&D Issues is shown in Figure 3. Specific categories of R&D issues and consequent planned activity areas are identified in the figure. To achieve these goals, the strategy is broken down into four distinct areas:

#### ● Research and Development

DOE/FETC is sponsoring a multitude of R&D contracts with industry, academia, nonprofit institutions and government laboratories that support the goals of the IGCC program. Research activities include *advanced gasifier* designs that have the potential to reduce capital and O&M costs, improve thermal efficiency, and process alternative feedstocks. The transport gasifier is being developed through a coordinated program utilizing several research facilities. One of the focus areas of this research is refractory materials and instrument development to improve gasifier performance, operational control, and reliability. Researchers are also developing fluid dynamic data and advanced computational fluid dynamic models to support the development of the transport gasifier and desulfurizer. The use of biomass and municipal waste as gasifier feedstocks for power and coproduction applications are being evaluated. Novel technologies for *gas cleaning and conditioning* are being developed to reduce capital and operating costs and to meet the stringent requirements for cogeneration and coproduction applications. These new technologies are needed to assure the supply of ultra-clean gas for fuel cell and catalytic conversion of syngas to fuels and chemicals as well as enabling advanced processes to effectively separate CO<sub>2</sub>. These technologies focus on minimizing consumables and waste products. Research is also being conducted in the area of *advanced gas separation* technologies with the goals of reducing both capital and operating costs, improving plant efficiency, and concentrating and capturing CO<sub>2</sub>. Researchers are investigating novel hydrogen separation technologies which are capable of operating at high temperatures and pressures and in the presence of chemical and particulate contaminants. New air separation technologies, such as mixed conducting ceramic membranes, for producing lower cost oxygen are also being developed. And lastly, technologies that can generate *value-added products* to minimize waste disposal and improve process economics are being evaluated. Processes that will improve the quality of the ash, slag, and sulfur by-products from the plant are being developed because adding value to these products will not only enhance the plant revenues, but will more effectively use all of a resource with less waste.

#### ● Systems Engineering and Analyses

A variety of economic analyses, process performance assessments, and market studies are being conducted to provide sound engineering and economic guidance for future R&D initiatives and to support commercialization activities, both domestically and internationally. Some examples include: an IGCC

optimization study for baseload power, cogeneration of steam, and coproduction of power and transportation fuels. These studies will help to define future R&D efforts and will provide the lowest cost and highest efficiency approaches. The R&D efforts can then be aimed at: reducing material costs and consumables as well as total plant costs; a detailed market analysis and the development of a commercialization strategy tailored for coproduction applications; and system studies to assess the production, mitigation, and sequestration of CO<sub>2</sub> in IGCC applications for baseload power generation, cogeneration, and coproduction and concepts for achieving zero emissions and closing the carbon cycle.

- **Technology Integration/Demonstration**

Demonstrate gasification-based technologies at an industrially relevant scale of operation to confirm process scale-up, provide RAM data, and evaluate process performance. Activities would include providing DOE resources to insure the success of existing IGCC Clean Coal Technology programs through technical assistance and R&D projects. The scope of demonstrations will be expanded to incorporate fuel cell, turbine integrations, and hybrids and extend the versatility of demonstrated technology.

- **Product Outreach**

Funding for RD&D activities is becoming increasingly difficult to find in both the private and public sectors. In an effort to overcome these obstacles, DOE/FETC has implemented an aggressive outreach program to communicate, coordinate, and partner with anyone who has a stake in the outcome of IGCC RD&D efforts including: power generators; industrial firms; financial institutions; environmental groups; local, state, and Federal legislators; taxpayers, and others. As part of this activity, stakeholders will be educated on the technical, economic, and environmental benefits of the IGCC systems. Further outreach will be accomplished by coordinating activities with other Federal, state and local government programs and organizations whose programs are complementary to IGCC to avoid potential redundancies. Finally, the formation of multinational partnerships, consortia and user groups will assure a coordinated research effort and continued commercialization activities for gasification-based technologies.

## **ACHIEVING THE VISION**

By the year 2015, gasification-based technologies will have gained global acceptance and as a result will have penetrated worldwide power generation markets, achieved widespread use in the petroleum refining market, and attained, via coproduction, deployment in the fuels and chemicals market. Gasification-based processes will be the technology of choice by being the low-cost leader and providing superior environmental performance through modularity of design and fuel flexibility for easy integration into multiple applications. Commercial guarantees and financing will be readily available, therefore, minimizing the need for government incentives. This will result in improved U.S. industrial competitiveness and enhanced U.S. energy security through increased use of domestic resources. Beyond 2015, the Federal government will continue to develop advanced low-cost technologies to achieve America's goals of economic prosperity in multiple markets, energy security and environmental quality, leading toward zero discharge of all pollutants and greenhouse gases.

### **Early Entrance Coproduction Plants**

The versatility of coproducing power and fuels accelerates deployment of both IGCC and synthesis gas conversion technologies, increases capacity factor, and reduces risks. Coproduction would allow a reduction in oil imports by producing significant quantities of ultra-clean fuels from domestic resources with little or no carbon emissions. However, private investors and process developers are hesitant to invest in the design and construction of coproduction plants until technical, economic, and technology integration risks are acceptable. DOE is implementing a strategy to help mitigate these risks through the support of early entrance coproduction (EECP) small-scale commercial plants that will demonstrate the successful operation of the integrated technologies. They will be constructed adjacent to existing infrastructures, and be capable of processing multiple feedstocks and producing more than one product. These EECP plants will be built by an industrial consortia in partnership with state and federal governments. Once the identified risks have been shown to be acceptable by successful operation, future commercial plants would not require Federal funds for construction and deployment.

### **Vision 21**

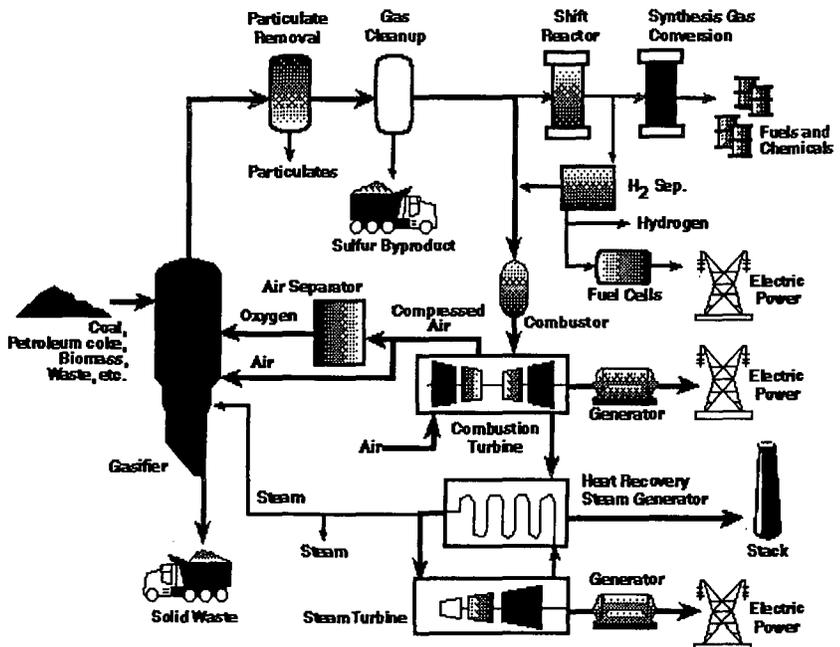
Ultimately, gasification will be the cornerstone technology for a new fleet of energy plants for the 21st Century, called Vision 21. These energy plants are highly efficient systems (greater than 60%) that will coproduce low-cost electric power, transportation fuels, and high-value chemicals, all tailored to the geographic energy market demands. The feedstock and product flexibility of gasification-based technologies, coupled with their high efficiency and ultra-low emissions, make them a core part of the Vision 21 concept.

Vision 21 is DOE's strategy for advancing the research and development of technologies critical to creating the integrated energy plants of the coming century. R&D by DOE and industry partners will focus on issues that are key to improving the efficiency, versatility and cost-effectiveness of IGCC components and systems, and to furthering synergies between IGCC and other advanced energy and environmental control technologies.

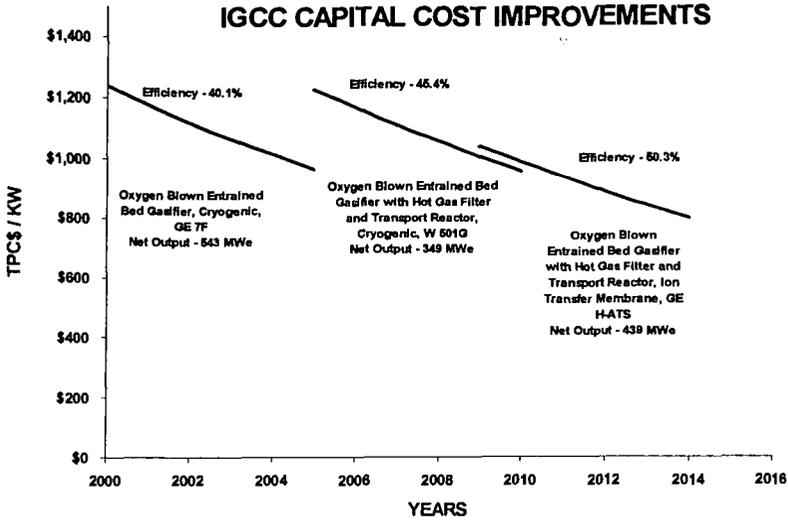
## CONCLUSIONS

Ultimately, IGCC could become the technology of choice for electric power generation. Improvements in IGCC performance are possible through continued development and integration of advanced technologies. Thanks to investments in energy research, development, and demonstration by the Federal government and industry partners, U.S.-based companies are poised for leadership in emerging world markets for IGCC systems, positioning them at the center of a vital energy industry in the 21st century.

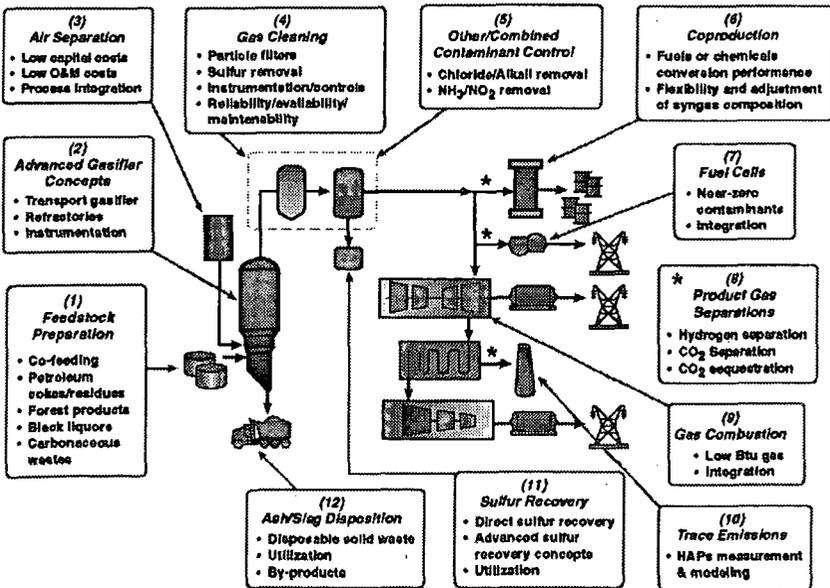
**FIGURE 1. INTEGRATION GASIFICATION COMBINED CYCLE**  
Technology Options



**FIGURE 2. POWER GENERATION  
IGCC CAPITAL COST IMPROVEMENTS**



**FIGURE 3. IGCC R&D ISSUES**



# STAGED COAL GASIFIER FOR POWER GENERATION AND FUEL PRODUCTION

**Atsushi Morihara,  
Fumihiko Kiso, Tooru Akiyama and Yasuo Yoshii**  
Hitachi Ltd.

**Fumihiko Hanayama**  
Babcock-Hitachi K.K.

**Satoshi Tsujiguchi and Junichi Iritani**  
Electric Power Development Co., LTD

## ABSTRACT

As coal is the most abundant fossil fuel, coal should be used for not only power generation but also production of fuel and agriculture chemicals. Staged coal gasifier can increase production of methane by controlling the feed oxidizer ratio between stages. The gasifier can also control the ratio hydrogen and carbon monoxide by feed steam to secondary stage. The gasifier can produce di-methyl ether easily at hydrogen production equal to carbon monoxide. The 50 tons per day pilot plant of the gasifier tested at Chiba prefecture in Japan from 1990 to 1995 by NEDO (The New Energy and Industrial Technology Development Organization). The main objective is production of Hydrogen. The new 150 tons per day pilot plant has started construction from 1998 by Electric Power Development Co., LTD. EAGLE (Coal Energy Application for Gas Liquid and Electricity) project aims to increase efficiency of staged gasifier and to achieve high performance clean up system.

## INTRODUCTION

Coal is the most abundant of the fossil fuels. At the end of 1990, proven world reserves of coal were estimated to be sufficient for more than 200 years at 1990 production rates. Its wide geographical distribution ensures that coal is to be found in every continent, and is fossil fuel in many countries.

Most coal used in power station. Coal-fired power stations generated almost 40% of the world's electricity. As coal is likely to remain a primary energy resource for the future environment concerns continue to dominate, these aspects will determine which technologies will be employed to convert coal in power. Therefore, that a great deal of effort is being directed into reducing the environmental impact of coal-fired generation through the environment of clean coal technologies.

Gasification processes produce fuel gas, which can be cleaned prior to firing in the turbine combustor, and suffer no such temperature constraint. In addition, there are many factors that make fuel gas easier to clean than gaseous combustion. Coal gasification is very old technology. Before natural gas was introduced on the market, coal gasification was used to produce fuel gas for distribution in urban areas. It has also been used quite frequently in the chemical and petrochemical industries to produce raw material for chemical process. Converting coal into clean fuel gas offers a very attractive way of generating power. That is used gas and steam turbines, with minimum environment impact.

Hitachi started research on the entrained flow coal gasification process in 1980, developed the two-stage gasifier, and then researched the basic coal gasification technology of the gasifier using 1-U/d process

development unit installed at Hitachi Researcher Laboratory in 1981.

The two-stage gasifier was adopted in 1986 as the coal gasification project of Japan sponsored by NEDO as a part of the Sunshine Project of MITI. Equipment development research was started using 3-t/d gasifier. HYCOL was established in 1986; it chose Hitachi's gasification process for its pilot plant. Hitachi group designed, fabricated, and constructed the 50t/d coal gasification pilot plant 1990[3].

The present paper addresses the continuation of that effort with the focus on the IGCC performance by using two-stage gasifier. This paper refers how to deal with molten slag and sticking fly ash, and show the effect on the total system performance on the focus decreasing of recycle gas.

## PRINCIPLE OF THE TWO-STAGE GASIFICATION PROCESS

The principle of the two-stage gasification process is shown in Fig. 1. Features of the process are as follows.

### (1) High gasification efficiency

Pulverized coal and oxygen, the gasification agent, are fed to upper and lower burners. They are tangentially installed on the gasifier in order to create a spiral flow in the gasifier. Enough oxygen is fed to the lower burners to melt down the ash contained in the feed coal. Pulverized coal fed to the upper burners is reacted at a lower temperature with a relatively smaller amount of oxygen, compared with that fed to the lower burner, and gasified and converted to reactive and less adhesive char. The char moves down along the spiral gas flow and mixes with high temperature gas in the lower portion of the gasifier, where gasification proceeds further. The produced gas is turned over and goes up to the exit of gasifier with a small amount of char.

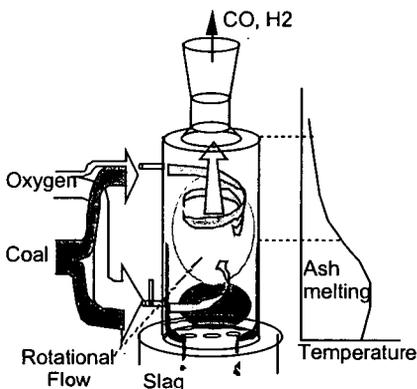


Fig. 1 Principle of the Two Stage Gasifier

The produced gas is turned over and goes up to the exit of gasifier with a small amount of char.

### (2) High thermal efficiency from a pneumatic feeding system

Pulverized coal is fed to the gasifier by a dense phase pneumatic feeding system using recycled gas or nitrogen. Therefore, a high temperature can be maintained with a small amount of oxygen, compared with the slurry feed system.

### (3) Reliable gasifier with a slag self-coated water-cooled tube wall.

The gasifier consists of a water-cooled tube wall, which is lined by a newly developed high temperature resistant castable. Molten slag solidifies on the inside surface of the wall at first and then molten slag flows down over the surface of the solidified slag. The slag self-coated system is more reliable and extends operation time, compared with the refractory lined gasifier.

### (4) Stable slag tapping

A pressure difference between the wall side and the center of the gasifier is generated by the spiral flow. Therefore, hot gas is recycled from slag taps to a gas tap. This ensures stable slagging of molten slag without burning auxiliary fuel.

For the purpose of estimation the two-stage gasification a computational fluids code has been developed for simulating coal gasifier.

## REACTION MODEL

Coal gasification is modeled as simultaneous de-volatilization and char gasification processes. The coal volatile is assumed to be a hydrocarbon mixture containing all of the coal hydrogen with the remaining mass being carbon. The volatile evolve at a rate expressed in Arrhenius form:

$$\frac{dV}{dt} = A_v \exp\left(\frac{-E_v}{T_p}\right) (V - V_{\max}) \quad (1)$$

Where  $A_v$  and  $E_v$  are kinetic rate constants,  $V$  is the fraction of coal evolved as volatile, and  $V_{\max}$  is the maximum volatile yield. Values of these parameters are shown in Table 1. Knill et al. (1989) showed that de-volatilization occurs during particle heating and is nearly instantaneous for particle temperature greater than 1300 K. Thus, the kinetic constants are chosen to ensure that de-volatilization is complete in 1 ms at 1300 K.

The remaining char is gasified with  $\text{CO}_2$  and  $\text{H}_2\text{O}$ :

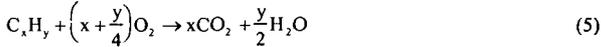


Both reactions are first order in the  $\text{CO}_2$  and  $\text{H}_2\text{O}$  partial pressures,  $P_{\text{CO}_2}$  and  $P_{\text{H}_2\text{O}}$ , and they proceed in parallel. The chemical reaction rates are expressed in Arrhenius form:

$$k_{c,i} = A_{c,i} \exp\left(\frac{-E_{c,i}}{T}\right) \quad (4)$$

Where the subscript  $i$  represents either  $c$  or  $h$ .

As the volatile is released from the coal, they react with oxygen to form complete combustion products.



The volatile reaction rate,  $R_v$ , is controlled by the mixing of fuel and oxidant according to the Eddy Dissipation Model (EDM) of Magnussen and Hjertager (1976). In the EDM, reaction rate is defined as the product of a characteristic eddy lifetime,  $k/\epsilon$  and the minimum of the volatile and oxygen mass fractions,  $Y_v$  and  $Y_o$ , respectively:

$$R_v = A_{edm} \frac{\epsilon}{k} \min\left(Y_v, \frac{Y_o}{r_o}\right) \quad (6)$$

Where  $r_o$  is the stoichiometry (mass  $\text{O}_2$ /mass volatile). The volatile combustion and char gasification products are redistributed in the gas phase according to these reactions:



The water/gas shift reaction and methane-steam reforming reaction may progress in either direction depending on gas composition and temperature as determined by equilibrium[4].

## CALCULATION RESULTS

Calculation results shown by fig 2. Cold gas efficiency increased with increasing upper oxygen ratio to coal, and with increasing lower oxygen ratio. The peak value of cold gas efficiency is given when addition of upper oxygen ratio to coal and lower equal 0.9. That shows cold gas efficiency is decided by total oxygen ratio of gasifier.

The outer gas temperature increase with increasing total oxygen ratio. The lower region temperature increases with increasing only lower oxygen ratio to coal.

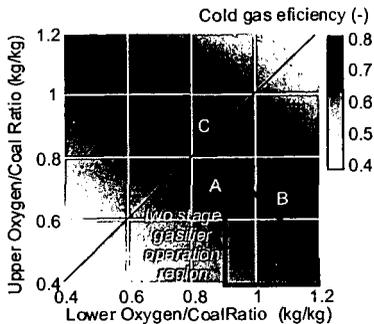


Fig. 2 Calculation Results of Two Stage Reaction

The operation region of oxygen ratio to coal at two-stage gasifier is described as below. To melt ash of coal, lower temperature need to be over ash melting point. Lower region of temperature is decided by lower oxygen ratio. Thus lower oxygen ratio need to be over the line A in figure 2.

On the other hand, the outer gas temperature is decided by total oxygen ratio. Total oxygen ratio need to be lower below the line B. Consequently operation region two-stage gasifier is shown as figure 2. The oxygen ratio to coal can be operated to be the maximum cold gas efficiency.

The oxygen coal ratio for the one stage gasifier depends on the temperature over than the melting point of coal. That is the oxygen feed operation need to be on the line C in figure 2. If the oxygen ratio to coal at the ash melting point is over than that given at the highest cold gas efficiency, the outer gas must increase. On the other hand the total oxygen ratio to coal does not have to be relate to the ash melting point at the two-stage gasifier. The two-stage gasifier can operate at lower oxygen concentration than one stage within some kinds of coal. Thus the two-stage gasifier can be operated in lower quench gas than the one stage gasifier.

## EAGLE PLANT

The new 150 tons per day pilot plant has started construction from 1998 by Electric Power Development Co., LTD. EAGLE (Coal Energy Application for Gas Liquid and Electricity) project aims to increase efficiency of staged gasifier and to achieve high performance clean up system.

Figure 3 shows gasifier and heat exchanger at EAGLE Project.

The EAGLE system consists of an oxygen-blown entrained flow gasifier; dry type coal feed system and wet gas clean-up system. The heating value of the coal gas produced by the oxygen-blown gasifier is comparatively high, and the gas quantity produced by processing coal is partial produced by an air blown gasifier.

In addition, in the dry coal feed system, since the coal is transported by dry gas, the latent heat loss due to evaporation of water is nearly eliminated and the water content in the coal gas is kept to a minimum. As a result of the above, losses incurred during the process of wet gas clean-up i. e. sensible heat loss of the coal gas,  $H_2O$  and  $CO_2$  losses are reduced. Therefore, a high heat efficiency system is expected[2].

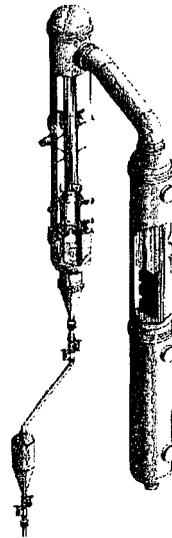


Fig3 Gasifier and Heat Exchanger

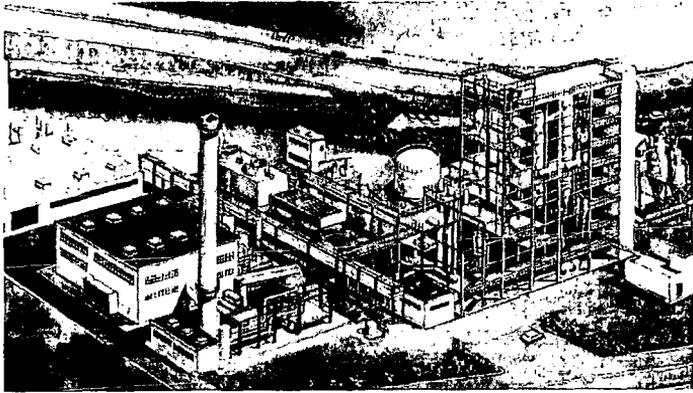


Fig4 Bird eye view of EAGLE Pilot Plant

## CONCLUSIONS

This paper has described the present status of developments in the Power Plant as a part of the developments on coal usage technology. The technology strives to achieve the same aim as clean coal technology.

## REFERENCES

- [1]K. Nomura et al "Development of the HYCOL Gasification Technology through Pilot Plant Operation" 13 th EPRI Conference on Gasification Power Plants, October 1994
- [2]T. Sasaki et al "Feasibility Study of an Integrated Coal Gasification Combined Cycle System with Oxygen-Blown Gasifier," Transaction of JASME 59,566(B), pp. 2660-2665(September 1993)in Japan
- [3]M. Takagi et al "Entrained flow Coal Gasification Development for a HYCOL Pilot Plant" Hitachi Review Vol. 44(1995),No. 1
- [4] FACT-Vol. 18 Combustion Modeling, Scaling and Air Toxins ASME 1994
- [5]M. Tsukamoto et al "Advances in Coal-fired Power Generation" Hitachi Review Vol. 44(1995),No. 1
- [6]H. Matsuoka et al "Development of the HYCOL Gasifier in the Pilot Plant Operation" 10 th. Annual International Pittsburgh Coal Conference(1994)

# INCREASING REACTIVITY OF ILLINOIS COAL FOR USE IN IGCC PROCESSES

Anthony A. Lizzio  
Illinois State Geological Survey  
615 East Peabody Drive  
Champaign, IL 61820

**Keywords:** coal gasification, IGCC processes, gasification reactivity

## INTRODUCTION

Integrated gasification combined cycle (IGCC) processes are expected to become an essential component for energy production in the next century. IGCC processes are able to utilize high sulfur coal and typically achieve power generation efficiencies in excess of 40%. The Illinois State Geological Survey (ISGS) has played an important role in the commercialization of IGCC technology in the Illinois Basin region [1]. A 400 ton test of Illinois coal initiated by the ISGS and performed with Destec Energy, Inc. at the Dow Chemical Plaquemine IGCC facility [2] in 1990, showed for the first time that Illinois coal, a caking coal, could be used effectively in this process. Continued use of Illinois coal at this facility, however, was not possible since the sulfur recovery unit at this plant was designed for low sulfur coal. The results from the 400 ton test, however, were used to help design the The Wabash River Coal Gasification Repowering Project in Terre Haute, IN, initially a joint venture between Destec Energy, Inc. and PSI Energy, Inc. and currently owned and operated by Dynegy Corporation. This ongoing commercial demonstration began operation in August 1995 and currently gasifies up to 2,500 tons/day of an Indiana coal to produce 262 MW of power [3]. The Wabash River facility is the first of its kind to utilize bituminous coal having moderate amounts of sulfur (1-2%). The sulfur in the coal is recovered as elemental sulfur, a saleable byproduct.

In the majority of IGCC processes (e.g., Texaco, Shell), coal is gasified in a one stage process at relatively high temperatures (1400°C) in an oxygen rich environment. In such a process, the coal delivered to the gasifier is converted to gaseous products within seconds, therefore, the intrinsic reactivity of the coal is not an important issue since mass transfer considerations dictate how fast the coal reacts. However, in a two-stage process such as the one being commercially demonstrated by Dynegy, coal is also gasified at lower temperatures (900-1000°C) in a mostly reducing atmosphere in the second stage gasifier. Leftover heat from the oxygen blown gasifier is recovered in the second stage by gasifying additional coal, up to 30% of the total feed. Since complete char burnout is rarely achieved in this second stage, the reactivity of the coal fed into the second stage becomes an important process consideration. If partially reacted char from the second stage is reintroduced into the first stage, this could lower the overall efficiency of the process since high ash, low BTU char now replaces some of the low ash, high BTU feed coal. The development of IGCC technology that utilizes a two stage process to gasify coal provides an opportunity to optimize the reactivity of the coal added to the second stage gasifier. A more reactive coal and resultant char would lead to higher levels of conversion in the second stage gasifier and more efficient operation. The use of more reactive coals in IGCC processes should lead to even more efficient production of electricity [4, 5].

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. Tar formation, which happens to be detrimental to IGCC process performance, could be suppressed by preoxidation as well as by the addition of calcium to the coal. The objective of this study [6, 7] was to evaluate and improve the gasification behavior of Illinois coal for use in two-stage IGCC processes. This commercial application precludes the use of alkali metal catalysts such as sodium or potassium since these may volatilize and damage the gas turbines. In this paper, we discuss various methods to increase char reactivity through coal preoxidation and/or addition of a suitable catalyst such as calcium or iron.

## EXPERIMENTAL

### Coal/Char Preparation

Coals were obtained from the Illinois Basin Coal Sample Program (IBCSP) [8] and from selected coal mines throughout Illinois. An Indiana coal currently being used in an IGCC two-stage gasifier was also studied. Coal chars were prepared from these coals in a 2 in. ID horizontal tube furnace (N<sub>2</sub>, 900°C, 30°C/min, 0.5 h). After pyrolysis, agglomerated chars were ground with a mortar and pestle to a -100 mesh particle size. Some coals were preoxidized in air at 225°C for 1 h prior to gasification tests and/or catalyst addition.

### Catalyst Addition

Calcium (acetate) and iron (chloride) were added to as-received coal by ion-exchange (IE) at different pHs. IE was conducted by shaking 250 mL of each metal solution with 1 g of coal for 24 h, after which the samples were filtered and the solids submitted for metal analysis. Ca and Fe were added by IE at their natural pH (5.5 and 2.0, respectively) or at pH = 10 by dropwise addition of NaOH. Gypsum was added to 250 ml of H<sub>2</sub>O containing 20 g of preoxidized coal and stirred at 60°C for 8 h. The pH of this mixture was adjusted to pH = 11.

## Coal/Char Gasification Reactivity

Two experimental procedures (isothermal and nonisothermal) were used to measure the gasification reactivity of the char or coal. The specific char gasification reactivity (g C/g C/h) as a function of char conversion ( $X_c$ ) in 1 atm  $\text{CO}_2$  at 850-940°C was determined by isothermal thermogravimetric analysis (TGA). The coal gasification rate as a function of time in 0.80 atm  $\text{CO}_2/0.20$  atm  $\text{H}_2\text{O}$  was determined by nonisothermal TGA (25-1000°C, 100°C/min). A Cahn TGA (TG-131) was used to monitor changes in char or coal reactivity with conversion or time. A typical isothermal experiment proceeded as follows. A char sample (10 mg) was placed in a platinum pan suspended from the Cahn weighing unit and enclosed by a Vycor hangdown tube. High purity nitrogen (99.999%) was introduced into the system (150  $\text{cm}^3/\text{min}$ ) and allowed to displace for 0.5 h the air in the reaction chamber. After flushing the system with  $\text{N}_2$ , the temperature was raised to 120°C and held for 15 minutes to record the dry weight. The sample was then rapidly heated (100°C/min) to the reaction temperature. Within 1 minute after reaching the setpoint, the temperature stabilized and the initial weight was recorded. High purity carbon dioxide (99.999%) was then introduced into the reaction chamber at the same flow rate (150  $\text{cm}^3/\text{min}$ ). Sample weights were recorded continuously at 30 s intervals until the run was terminated at 90-95% conversion. An ash determination was made for each sample by switching from the reactant gas to oxygen at the reaction temperature.

## **RESULTS AND DISCUSSION**

### Char Reactivity

Figure 1 presents typical reactivity profiles (specific gasification rate,  $R_p$ , versus conversion,  $X_c$ ) for IBC-101 char gasified in 1 atm  $\text{CO}_2$  at 850-940°C. Activation energies calculated from the Arrhenius plots for this char (Figure 2) increase slightly from 55.0 to 63.8 kcal/mol, well within values reported in the literature [9] for coal char gasification in  $\text{CO}_2$ . Thus, the reactivity profiles obtained for IBC-101 under these conditions are considered to be in the chemically controlled regime and represent true variations in char reactivity with conversion.

The gasification reactivities of chars prepared from nine of the twelve coals in the IBCSP were determined in 1 atm  $\text{CO}_2$  at 850 by isothermal thermogravimetric analysis. Chars were prepared in a tube furnace under identical pyrolysis conditions ( $\text{N}_2$ , 30°C/min, 900°C, 0.5 h) prior to the gasification tests. Figure 3 presents reactivity profiles for these coals and two other Illinois coals, Cedar Creek and Crown II coal, and the Indiana coal. Figure 3 shows that 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 most reactive and the high ash IBC-104 char and Indiana coal were the least reactive. Cedar Creek coal having more than twice the sulfur content (the more sulfur the better since sulfur can be recovered as a saleable byproduct), but less ash than the Indiana coal, was more than twice as reactive as the Indiana coal char. Char made from Crown II coal was nearly four times as reactive as the Indiana coal char. Another method of measuring reactivity involving rapid heating (100°C/min) of the coal sample in a reducing atmosphere (80%  $\text{CO}_2$ , 20%  $\text{H}_2\text{O}$ , 1 atm) was also used. The results from nonisothermal tests confirmed the order of reactivity obtained from these isothermal tests.

### Effect of Preoxidation

Perhaps the most cost effective way to increase the reactivity of bituminous coal would be to add oxygen to it prior to gasification either by natural weathering or a low temperature oxidation treatment. A recent study [10] has shown improved combustion performance for naturally weathered (oxidized) coals versus 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, which could lead to an increase in char reactivity [11]. Figure 4 presents reactivity profiles for several as-received and preoxidized coals. Preoxidation of IBC-102 and Cedar Creek coal results in little or no increase in reactivity. Preoxidation of the Indiana coal actually leads to a decrease in reactivity. Coal preoxidation also reduces the BTU content of the coal, which would decrease overall process efficiency. Thus, coal preoxidation alone does not appear to be a viable means to increase the gasification reactivity of these candidate coals for the Wabash River gasification plant.

### Catalyst Addition

Calcium and iron are appropriate catalysts for the strict corrosivity requirements of IGCC processes. Abotsi et al. [12] recently evaluated the uptake of iron by coal particles dispersed in water. A surfactant, sodium dodecylsulfate, was used to increase the dispersion and stability of iron loaded onto an Illinois #6 coal. Iron loadings up to 3 weight percent were achieved. Adsorption of iron and calcium onto coal occurs through exchange of the cations ( $\text{Fe}^{+2}$ ,  $\text{Ca}^{+2}$ ) with the protons on the carboxylic or phenolic acidic groups on coal. The use of a surfactant promotes the dissociation of the surface functional groups, which creates a negative charge on the surface of the coal. This will favor adsorption of  $\text{Fe}^{+2}$  through electrostatic interaction between  $\text{Fe}^{+2}$  and negatively charged active sites. Practically speaking, efficient catalyst adsorption and dispersion in the coal would need to occur during transport of a coal-water slurry to the gasifier.

The effects of calcium and iron on the gasification behavior of Illinois coal were examined. Calcium and/or iron were added to IBC-101, Crown II, IBC-102, and Indiana coal by ion exchange at various pHs (2.2, 5.6 and 10) to determine to what extent these catalysts would impact char reactivity. Figure 5 presents reactivity profiles (conversion versus time) for Ca- and Fe-catalyzed IBC-101 chars gasified in 1 atm CO<sub>2</sub> at 850°C. When Ca is added by IE at pH = 10, there is a three-fold increase in reactivity. Iron added by IE at pH = 2.2 (natural pH) is seen to have little impact on reactivity. On the other hand, Fe added by IE at pH = 10 increases reactivity by more than a factor of two. These results indicate the importance of using an alkaline medium for preparing Ca- and Fe- catalyzed coals by IE. To the best of our knowledge, no one has shown that adjusting pH during catalyst loading can enhance subsequent reactivity of the catalyzed char. Figure 6 presents reactivity profiles for Crown II coal chars gasified in 1 atm CO<sub>2</sub> at 850°C. The as-received Crown II coal was our most reactive Illinois coal (Figure 3). When Ca or Fe is added to this coal by IE (at pH = 10), char reactivity again increases by more than a factor of two. The reactivities of these coals prepared at their natural pH (either 5.6 or 2.2) are significantly lower than those at pH = 10, consistent with results obtained for the catalyzed IBC-101 coals (Figure 5). Figure 6 presents reactivity profiles for the Indiana coal char. Addition of Ca and Fe at pH = 10 leads to only a slight increase in reactivity. Addition of Ca at its natural pH (5.6) actually decreases reactivity. These results indicate that Illinois coals are not only more reactive than the Indiana coal, but also respond better to the catalyst treatments perhaps due to a more favorable surface chemistry, i.e., greater amount of carbon-oxygen groups that facilitate ion-exchange between the catalyst and the carbon surface.

#### Effect of Coal Preoxidation on Catalytic Activity

Crown II and IBC-102 coal were preoxidized prior to catalyst addition to determine the effect, if any, of preoxidation on catalytic activity. Although preoxidation in itself was not an effective means to increase char reactivity (Figure 4), coal preoxidation prior to catalyst addition by IE would likely provide additional ion exchange sites for calcium or iron to react with. The coal samples were preoxidized by exposure to air at 225°C for 90 min before catalyst addition by ion exchange using calcium acetate. Figure 8 shows the effects of preoxidation and pH on reactivity profiles of Ca-catalyzed IBC-102 chars gasified in 1 atm CO<sub>2</sub> at 850°C. The reactivity of preoxidized IBC-102 coal is similar to that of the as-received coal. When Ca is loaded by IE at pH = 11 the maximum rates for both the Ca-catalyzed raw coal and preoxidized coal chars (between 6.5 and 8.3 g/g/h) are significantly higher than that of the raw coal (1 g/g/h). The increase in reactivity is more pronounced for the preoxidized sample (8.3 g/g/h). Both Ca-catalyzed chars maintain the high reactivity over most of the conversion range ( $X_c = 0.15 - 0.80$ ). In addition, the Ca-catalyzed chars prepared at their natural pH (5.6) was not as reactive as the one prepared at pH = 11 indicating once again the importance of pH during catalyst preparation.

Figure 9 shows the effects of preoxidation and pH on the reactivity profiles obtained for Ca-catalyzed Crown II chars gasified in 1 atm CO<sub>2</sub> at 850°C. The preoxidized Crown II coal was less reactive than the as-received coal. When Ca is loaded by IE at pH = 11 on the as-received and preoxidized Crown II coal, the gasification rates of both chars increase dramatically. The Ca-catalyzed preoxidized Crown II char maintains its high reactivity to higher levels of conversion compared to the Ca-catalyzed as-received coal indicating better dispersion of the catalyst in the preoxidized sample. The increases in reactivity are not as dramatic when the catalyst is loaded at its natural pH = 5.6, which is consistent with the trends observed for IBC-102 coal (Figure 8). From the data presented in Figures 8 and 9, it appears that oxidation of the coal prior to catalyst addition had a positive effect on the reactivity of both IBC-102 and Crown II coals. Figure 10 shows non isothermal reactivity profiles for raw, preoxidized, Ca-catalyzed raw, and Ca-catalyzed preoxidized IBC-101 coal. Less volatile matter is given off during the pyrolysis stage (24-45 min) for the preoxidized coal and the reactivity of the raw and preoxidized chars are comparable (56-68 min). The Ca-catalyzed chars begin to gasify at a much earlier temperature (about 200°C) than the uncatalyzed chars. The catalyzed preoxidized char produces less volatile matter during the pyrolysis stage than the catalyzed raw coal, which would be expected based on the reactivities of uncatalyzed raw and preoxidized chars.

#### Use of Gypsum as a Catalyst Precursor

Although calcium acetate is an effective catalyst precursor, its cost may be too high to justify its use in IGCC processes. We also attempted to load calcium onto Crown II coal by ion exchange using gypsum (calcium sulfate) instead of calcium acetate. Figure 11 shows clearly the catalytic effect imparted by gypsum to preoxidized Crown II coal at pH = 11. This result was rather unexpected given the relatively low solubility of gypsum in water (2 g/L) versus calcium acetate (> 80 g/L). Gypsum-catalyzed char is about one half as reactive as calcium acetate-catalyzed char and several times more reactive than the preoxidized coal char. One would expect very little increase in reactivity based on the solubility of gypsum, however, it appears that a significant amount of calcium was incorporated into the coal. This probably occurs because gypsum continues to solubilize as calcium is ion exchanged onto the coal, thus maintaining a sufficient driving force for the ion exchange process. This so-called "shuttling" of calcium from gypsum to coal leads to substantial loadings of calcium given a sufficient amount of time. An increase in the amount of soak time from 8 h to say 48 h as well as optimizing pH of the solution could further increase calcium loadings achieved by gypsum. Figure 12 presents non isothermal reactivity profiles for gypsum-catalyzed chars prepared at pH = 5.6 and pH = 11. The catalyzed coal prepared at pH = 11 is significantly more reactive than the raw coal or catalyzed coal prepared at pH = 5.6. Volatile matter production of the pH = 11 char during pyrolysis is also noticeably less than that of the other two chars. The effects of pH (11

versus 5.6) and catalyst precursor (gypsum versus calcium acetate) on the reactivity of Crown II coal char are shown in Figure 13. Calcium acetate loaded coal is still more reactive than gypsum loaded coal. Perhaps an increase in soak time and/or a more suitable pH will narrow the gap between CaSO<sub>4</sub> and CaAc. Figure 14, shows the effect of calcium precursor on so-called tar formation or volatile matter evolution. Gypsum catalyzed coal produces significantly less volatile matter (part of which is comprised of tars) than the calcium acetate loaded coal

Possible benefits to be derived from using gypsum instead of other catalyst precursors include: 1) a cheap, readily source of catalyst is made available, 2) a new use is found for gypsum, a coal combustion by-product, 3) sulfur from the gypsum could be recovered as a valuable by product in post gasification cleanup processes, 4) calcium oxide would be converted to calcium carbonate, thus reducing emissions of carbon dioxide from the gasifier, and 5) calcium would suppress tar formation, which is detrimental to the performance of some gasifier systems. Dynegy adds limestone to the coal water slurry prior to gasification to improve the slagging behavior of the ash. The limestone, however, is essentially inert with respect to increasing reactivity. Along these same lines, SASOL, the operator of the largest single train gasification plant in the world, is experimenting with adding catalysts to their feed coal to increase coal throughput in their process [13]. SASOL is using a waste stream from a power plant that contains low concentrations of calcium and sodium as the catalyst precursor solution. Note that the calcium originates from gypsum present in the power plant waste water. An up to three-fold increase in reactivity was observed when their feed coal was allowed to soak in this solution [13]. SASOL operates eighteen fixed-bed Lurgi gasifiers to produce chemicals by Fischer-Tropsch synthesis.

#### Potential Use of Illinois Coal in IGCC Processes

Table 1 presents key gasification properties of both Illinois and Indiana coals. The % ash, % sulfur, heating value of some of the more promising coals in these two states shows that several Illinois coals have more favorable properties than the Indiana coal presently being gasified at the Wabash River gasification plant. Cedar Creek coal apparently has the most favorable combination of properties with respect to ash content (6.00%), sulfur content (3.8%) and heating value (12,271 BTU/lb). Table 1 also lists the gasification rates at 20% char conversion in 1 atm CO<sub>2</sub> at 850°C. The Crown 2 coal is seen to be most reactive Illinois coal, while Pattiki is the least reactive. The Indiana coal is the least reactive among all the coals listed. Another important property of the coal is its T<sub>250</sub> value, which is based on the composition of the ash and gives a good indication of its slagging behavior. These values have been calculated for each coal using a graphical correlation [14] and are also listed in Table 1. Any coal having a T<sub>250</sub> value less than 2350°F can be gasified without having to add limestone. Dynegy typically adds limestone to their coal/water slurry feed to modify the slagging behavior of the ash. If little or no limestone needs to be added, a significant savings in operating cost could be realized. It is interesting to note that the T<sub>250</sub> of the Industry mine coal is less than 2150, which is quite favorable for use in the Wabash River IGCC process. It is also important that the mineral matter content of the coal feed be as low as possible. Low ash coal means less waste disposal; less energy is required to heat the coal since ash also contains water that needs to be vaporized. The sulfur content of the Indiana coal is relatively low (1.71%) compared to what would work best in the sulfur recovery system. A coal with twice the sulfur content would be easily handled by the Dynegy system. Several tests with coals other than the one presently being using are planned in the near future. The coals to be tested, however, have not been decided. High sulfur (6%) petroleum coke is also being tested.

Table 1. Comparison of Illinois and Indiana coals.

	% ash	% S	T <sub>250</sub> (°F)	R <sub>sp</sub> <sup>1</sup> (h <sup>-1</sup> )	BTU/lb <sup>2</sup>	FSI <sup>3</sup>
Illinois coals						
IBC-101	10.40	4.40	---	0.25	10,764	3.8
IBC-106	8.90	3.80	---	0.13	11,796	4.3
IBC-112	10.80	2.80	---	---	12,425	6.5
Crown 2	8.72	4.14	2,500	0.35	11,022	3.5
Industry Mine	7.07	3.58	< 2,150 <sup>3</sup>	0.16	11,500	2.5
Cedar Creek	6.00	3.68	< 2,630 <sup>3</sup>	0.16	12,271	3.0
Monterey 2	9.63	4.20	2,500	0.14	11,183	4.0
Old Ben 25	9.36	3.12	2,460	0.12	12,163	4.5
Pattiki	9.27	3.13	2,410	0.09	11,959	4.0
Eagle 2	9.57	3.32	2,420	---	11,867	4.5
Indiana coal	10.53	1.71	---	0.06	10,805	---

<sup>1</sup> char gasification rate at 20% conversion in 1 atm CO<sub>2</sub> at 850°C.

<sup>2</sup> corrected for equilibrium moisture.

<sup>3</sup> the predicted temperature is below the temperature of critical viscosity, thus the graphical correlation used is not applicable, actual T<sub>250</sub> is less than the given temperature.

## SUMMARY

The goal of this study was to provide Dynegy Corporation (formerly Destec Energy) with sufficient data to perform a large scale test with Illinois coal, either as received or modified by preoxidation and/or catalyst addition. An analyses of thirty four coals obtained from active mines throughout Illinois showed that several had lower ash content, higher sulfur content and heating value than the Indiana coal presently used by Dynegy. The Indiana coal char was the least reactive 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. Coal preoxidation had minimal effect on gasification reactivity of Illinois and Indiana coals. Coal reactivity was enhanced by adding catalysts (Ca or Fe) under conditions simulating those of a coal/water slurry. Catalytic effects were strongly dependent on the pH (> 10) of the ion exchange medium. 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. Although coal preoxidation was not an effective means to increase char reactivity, preoxidation of the coal prior to catalyst addition enhanced the reactivity of the Ca-catalyzed coal by providing additional ion exchange sites. The use of gypsum ( $\text{CaSO}_4$ ), a coal combustion by-product, instead of calcium acetate (CaAc), as a catalyst precursor was studied. The reactivity of gypsum-catalyzed char was significantly greater than that of uncatalyzed char, but less than one prepared using calcium acetate. The catalytic effect imparted by gypsum was surprising given that gypsum has a relatively low solubility compared to calcium acetate. Further work is needed to modify and test Illinois coals for use in IGCC processes. Binary catalyst systems, which have shown considerable promise in lower temperature gasification systems may provide superior performance relative to equivalent loadings of a single catalyst. Large scale tests need to be performed using ton quantities of optimized Illinois coal under process conditions simulating those used in the Dynegy entrained flow gasifier. The possibility of using Illinois coal in other IGCC processes such as the one to be demonstrated at the Grand Tower Power Station built in Southern Illinois [15] also needs to be examined.

## ACKNOWLEDGEMENTS

Funding for this work was provided by the Illinois Clean Coal Institute through the Illinois Department of Commerce and Community Affairs. The technical assistance of Deepak Tandon, Mark Cal, Gwen Donnals, Sheila Desai and Gwen Murphy is gratefully acknowledged. Discussions with Albert Tsang, John Lytle, Ilham Demir and Dan Banerjee are much appreciated. Special thanks to Godfried Abotsi and Gautam Saha for preparing Ca and Fe catalyzed Illinois coal chars.

## REFERENCES

1. Ehrlinger, H.P., Lytle, J.M., Breton, D.L., Lizzio, A.A. and Honea, F.I., 1992, "Gasifier Feed-Tailor- Made from Illinois Coal," Final Technical Report to the Illinois Clean Coal Institute.
2. Roll, M.W., Strickland, D.T. and Payonk, R.J., "The Destec Coal Gasification Process at LTGI," 1993, Proceedings of Tenth Annual International Pittsburgh Coal Conference, p. 333.
3. Roll, M.W., "The Construction, Startup and Operation of the Repowered Wabash River Coal Gasification Project," 1995, Proceedings of Twelfth Annual International Pittsburgh Coal Conference, p. 72.
4. Ahn, D.-H., Kim, J.-J., Kim, N.-H., Park, H.-Y. and Kim, C.-Y., "A Study on the Impacts of Changes in Coal Quality on the Performances of Gasification Processes and IGCC," 1995, Proceedings of Twelfth Annual International Pittsburgh Coal Conference, p. 187.
5. Farina, G.L., "The IGCC European Scene," 1995, Proceedings of Twelfth Annual International Pittsburgh Coal Conference, p. 199.
6. Lizzio, A.A., Cal, M.P., Lytle, J.M., Demir, I., Donnals, G.L., Breton, D.L., Tsang, A. and Banerjee, D.D., 1997, "Methods to Evaluate and Improve the Gasification Behavior of Illinois Coal," Final Technical Report to the Illinois Clean Coal Institute.
7. Tandon, D. Lizzio, A.A., Abotsi, G.M.K. and Saha, G., 1997, "Increasing Reactivity of Illinois Coal for Use in IGCC Processes," Proceedings of Twenty Third Biennial Conference on Carbon, University Park, PA, p. 454.
8. Demir, I., Lizzio, A.A., Fuller, E.L. and Harvey, R.D., 1994, "Evaluation of the Surface Properties of Illinois Basin Coals," *Journal of Coal Quality* 13, p. 93.
9. Lizzio, A.A., Jiang, H. and Radovic, L.R., 1990, "On the Kinetics of Carbon (Char) Gasification: Reconciling Models with Experiments," *Carbon* 28, p. 7.
10. Pisupati, S.V., Ph.D. Thesis, The Pennsylvania State University, 1991.
11. Mahajan, O.P., Komatsu, M. and Walker, P.L. Jr., 1980, *Fuel* 59, p. 3.
12. Saha, G., Bota, K.B. and Abotsi, G.M.K., "Assessment of Catalyst-Containing Coal-Water Slurry Formulations," 1995, Proceedings of Twenty Second Biennial Conference on Carbon, San Diego, CA, p. 502.
13. Prinsloo, F.F. and Schneider, M., 1997, "Kinetics of Catalyzed CO<sub>2</sub> Coal Gasification Reactions, Twenty Third Biennial Conference on Carbon, The Pennsylvania State University, University Park, PA, p. 426.
14. Demir, I., Harvey, R.D., Ruch, R.R., Chaven, C., Damberger, H.H., Steele, J.D., Frankie, W.T. and Ho, K.K., 1993, "Characterization of Available Coals from Illinois Mines," Final Technical Report to the Illinois Clean Coal Institute.
15. Clean Coal Today, Newsletter published by U.S. Department of Energy, Spring 1999, p. 1.

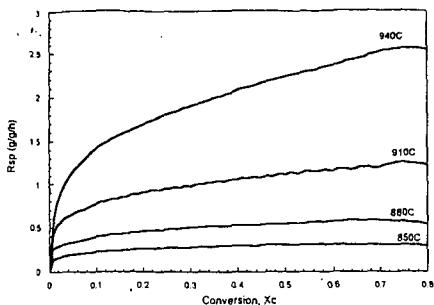


Figure 1. Reactivity profiles for IBC-101 char gasified in 1 atm CO<sub>2</sub>.

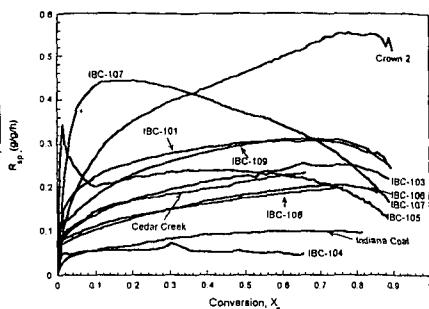


Figure 3. Reactivity profiles for Illinois and Indiana coal chars gasified in 1 atm CO<sub>2</sub> at 850 °C.

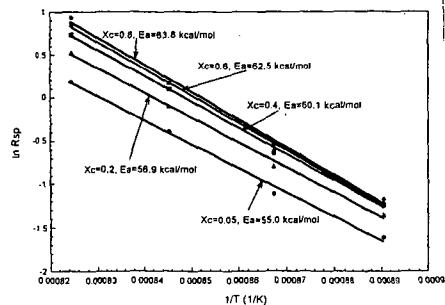


Figure 2. Arrhenius plots for IBC-101 char.

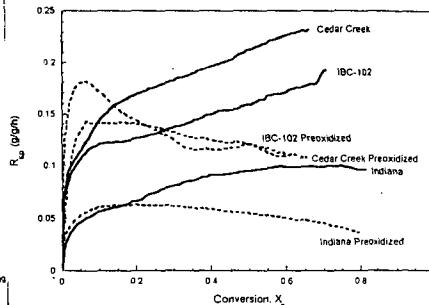


Figure 4. Effect of preoxidation (air, 225 C, 1h) on gasification reactivity.

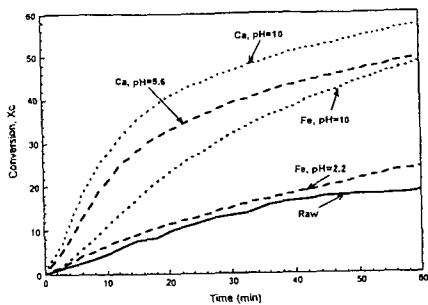


Figure 5. Effect of pH and catalyst on gasification reactivity of IBC-101 char.

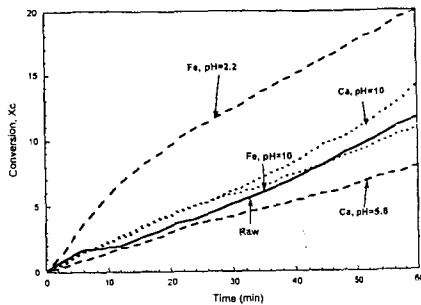


Figure 7. Effect of pH and catalyst on gasification reactivity of Indiana char.

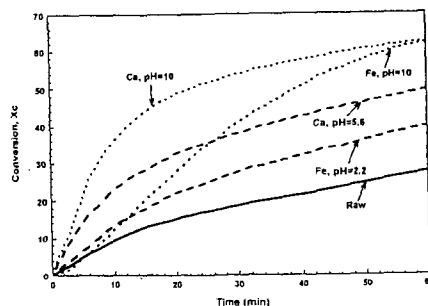


Figure 8. Effect of pH and catalyst on gasification reactivity of Crown II char.

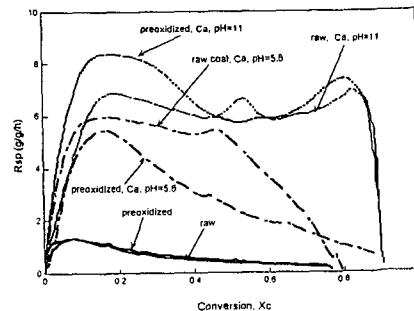


Figure 6. Effect of preoxidation and pH on reactivity of Ca-catalyzed IBC-102 char.

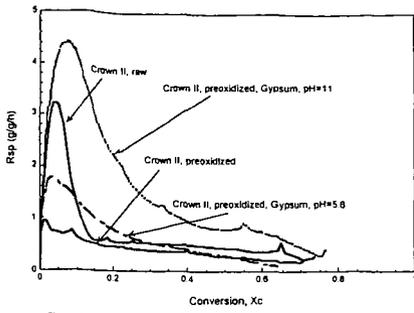


Figure 11. Use of gypsum ( $\text{CaSO}_4$ ) as catalyst precursor.

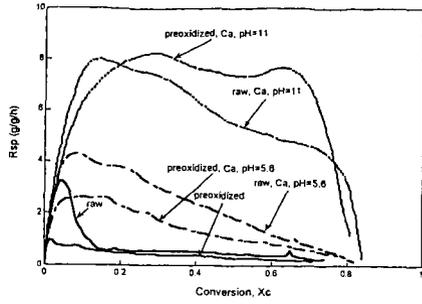


Figure 9. Effect of preoxidation and pH on reactivity of Ca-catalyzed Crown II char.

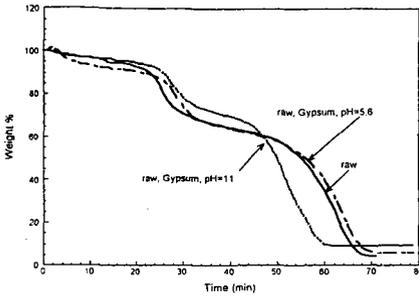


Figure 12. Effect of gypsum and pH on non isothermal reactivity of raw IBC-102 coal.

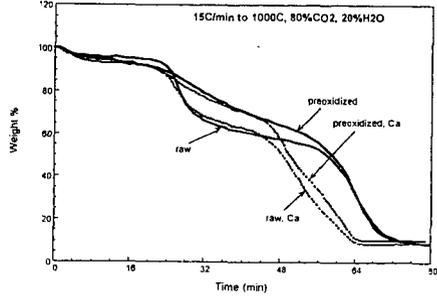


Figure 10. Effect of preoxidation and calcium addition on non isothermal reactivity of IBC-101 coal.

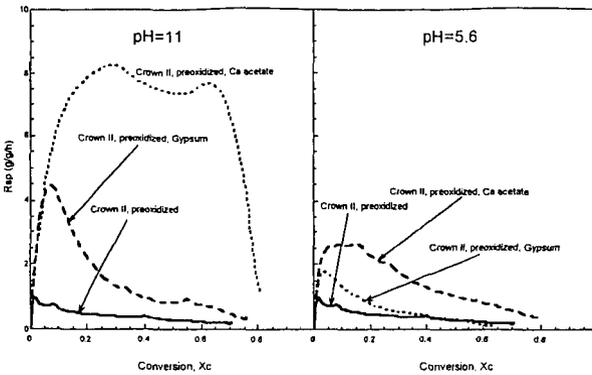


Figure 13. Comparison of gypsum and calcium acetate.

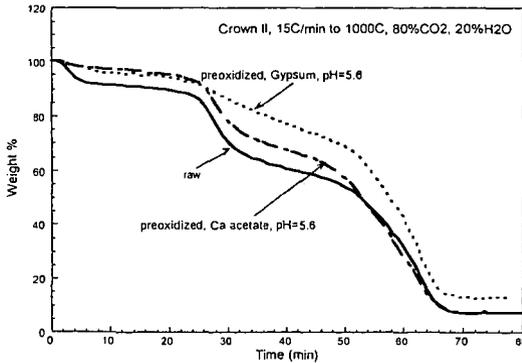


Figure 14. Effect of catalyst precursor on tar formation.

## **CHEMICALLY ACTIVE AEROGELS FOR HOT GAS CLEAN-UP IN A IGCC PROCESS**

Uschi M. Graham and Gerald Thomas. University of Kentucky, Center for Applied Energy Research, 2540 Research Park Drive, Lexington, KY 40511 - 8410.

### **Abstract**

To aid the development of IGCC technologies, the unique properties of aerogels were exploited to research purifying systems for  $H_2S$ ,  $NO_x$  and Hg that are durable and efficient. Aerogels can be used to capture hot gases based on their high surface areas and great tendency to form composites with various other sorbents or structural supports. Silica aerogels are at the heart of the study. Sol-gel synthesis achieved chemically active silica aerogels which were used as structural supports for diverse catalysts depending on the type of gases. Carbon aerogels are also included, focusing mainly on  $H_2S$  (g) sorption. Varying the nano- and microstructure of the aerogels and supported metal catalysts further aids in the hydrogenation of  $CO_2$  and selective catalytic reduction of  $NO_x$ . Among the sol-gel composite materials applied in this study, those being composed of both organic and inorganic components (organic-inorganic hybrid composites) are observed to have particularly strong affinities for mercury thereby achieving an effective mercury control.

**Keywords:** aerogels, micro-structure, adsorption

### **Introduction**

Today, coal supplies more than 55% of the electricity consumed in the United States, and it is likely to remain the dominant source of fuel for electric-power generation well into the next century. Integrated gasification-combined-cycle (IGCC) technology is one of the most promising new prospects for electricity from coal to emerge in recent years. It is one of the cleanest methods of generating coal-fired electricity. Rather than burning coal directly, the IGCC technology begins by converting the coal into a combustible gas. The gas itself can be stripped off its impurities, a process capable of reducing about 95% of the sulfur in coal. In addition the technique removes about 90% of the nitrogen oxide pollutants. Because of the IGCC's higher efficiencies in producing electricity compared with conventional coal power plants, a given amount of fuel will produce correspondingly less greenhouse gas leading to a reduction of carbon dioxide gas by at least 35%. However, the gasified coal also contains sizable quantities of hydrogen sulfide ( $H_2S$ ), a rather toxic gas that also has undesirable corrosive effects on the pipes and turbines. Various sulfidation mechanisms have been suggested during the absorption of  $H_2S(g)$  by bulk sorbents, or by a novel concept involving the conversion of  $H_2S(g)$  to  $H_2(g)$  and elemental sulfur by applying electrochemical membranes.<sup>1</sup>

Previous studies demonstrated different ways of cleaning the acid gas emissions prior to burning in a combustion turbine, including  $SO_2$ ,  $NO_x$  and  $CO_2$  by converting them into marketable commodities including sulfur, sulfuric acid, gypsum and fertilizers.<sup>2</sup> Although the bulk of the pollutants can be effectively controlled, there is still much uncertainty over the technically most effective approach for controlling mercury emissions and also on how to capture those small amounts of residual  $H_2S(g)$  which escaped from the primary recovery phase.

The dominant source of anthropogenic mercury emissions in the United States is derived from coal since conventional particulate control devices can not capture mercury in either of its gaseous forms ( $Hg^0$ ;  $Hg^{2+}X$ ) effectively. The Environmental Protection Agency (EPA) estimated that mercury from power plants accounts for 45 % of the total 158 tons/yr.<sup>3</sup> During coal gasification mercury is completely volatilized and a promising approach for mercury control is the injection of an effective sorbent. New IGCC technologies need to address an effective mercury control and previously obtained data for mercury sorbent developments designed for coal fired boilers provide a vast source of information.<sup>4-5</sup> Recent findings<sup>6</sup> indicated a poor sorbent performance of mercury on activated carbon substrates in the presence of the acid gases  $SO_2$ , HCl, NO, and  $NO_2$ , a typical gas mixture always to be expected during gasification of coal. The interaction of  $SO_2$  and  $NO_2$  was observed to be particularly detrimental on the sorbent performance. For example  $NO_2$  in a simulated flue gas inhibits  $Hg^0(g)$  adsorption on activated carbon but promotes the formation of  $Hg^{2+}X$  (e.g., X corresponds to  $Cl_2(g)$  or  $O(g)$ ; mercuric solids are possible in the presence of sulfate and sulfide) instead which occurs at  $NO_2(g)$  concentrations as low as 20 ppmv.<sup>7</sup> Although the mechanisms of the mercury-sorbent-interaction in the presence of  $SO_2$  and  $NO_2$  are not understood it is known that the  $Hg^0(g)$  typically is converted to a volatile oxidized form and it is suggested that the sorbent's oxidized surfaces catalyze the reaction.<sup>8-9</sup> Since the IGCC technology helps eliminate fly ash emissions completely, the interactions between  $Hg^{2+}X$  and fly ash particle surfaces and, hence, any respective surface-catalytic effects typically occurring during flue-gas/fly ash interactions can be neglected for the purpose of this investigation. Experimental results from the sorbent-mercury-flue gas interactions may be extrapolated to the IGCC system.

In the case of mercury, carbon sorbents have been used with varying success because of the interfering reactions mentioned earlier. However, in case of  $H_2S(g)$ , carbon sorbents offer excellent recovery potential from the hot flue-gas stream even under a wide range of different operating conditions. It has also been suggested that the carbons may be used as an active support for either copper or zinc oxides to further enhance the sorption process.<sup>10</sup> Instead of injecting activated carbon as a sorbent in a IGCC system this study focuses on the unique properties of advanced aerogel materials.

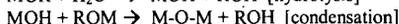
### Objectives

Experiments are performed to capture both mercury and hydrogen sulfide, but not necessarily on the same aerogels. The overall objective is to identify conditions for effective capture using chemically active aerogels (and aerogel composites). Applications for aerogel materials include additives for advanced composite materials, such as more reactive sorbents. It is the study's primary objective to observe the affinity of chemically enhanced aerogels towards capturing gaseous mercury species even in the presence of a typical flue gas mixture including  $NO_2$  and  $SO_2$ . Another approach focuses on scrubbing dilute quantities of  $H_2S(g)$ .

### Materials

Aerogels are highly porous, semi-transparent metal oxide materials.<sup>11-12</sup> They are very light (the lightest have a density of only 3 times that of air, i.e.  $0.003\text{ g/cm}^3$ ) and are characterized by excellent heat resistance (up to  $800\text{ }^\circ\text{C}$ ), an important property allowing us to use aerogels to clean hot flue gas emissions. They have extremely high surface areas ( $600\text{-}1000\text{ m}^2/g$ ) and are the product of supercritical drying of a sol-gel produced alcogel.<sup>13, 14, 15</sup> The combination of their properties makes them attractive for a number of reasons to be used in the adsorption and safe storage of pollutants from IGCC processes.

A thorough review of the sol-gel process used in this study, describing the transition of a system from liquid, mostly colloidal, into a solid gel phase can be found elsewhere.<sup>16-17</sup> In general, the sol-gel chemistry is based on the hydrolysis and condensation of metal alkoxides  $M(OR)_z$ . These reactions can be generalized as follows:



The silica aerogel pore network can be characterized by an open-pore structure. The flue gas can flow from pore to pore, and eventually through the entire aerogel. It is this property that makes aerogels effective sorbents for gas phase infiltration and reaction. Although the silica aerogels possess pores in the micro, meso, and macro size range, the majority of the pores fall in the mesopore regime (diameters between  $2\text{-}50\text{ nm}$ ). The carbon aerogel also has predominantly meso pores with a slightly larger pore radius and pore sizes  $>100\text{ nm}$ . The pore size distribution of the silica and carbon aerogels used in this study are shown in Figure 1.

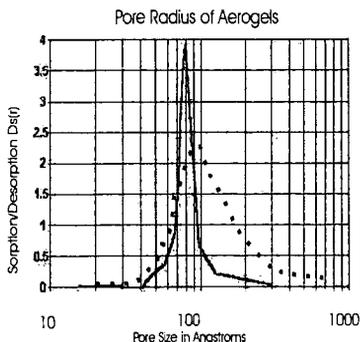


Figure 1 illustrates the distribution of pore radius for a silica aerogel (solid curve) and for a carbon aerogel (dotted curve).

Carbon aerogels are composed of covalently bonded, nanometer-sized particles that are arranged in a 3-dimensional network. Unlike conventional carbon blacks that are produced from gas phase reactions,

these materials are derived from the sol-gel polymerization of selected organic monomers in solution. After the solvent was removed, the resultant organic aerogel was pyrolyzed in an inert atmosphere at 600 °C from 45 minutes to form a carbon aerogel. This material has high porosity (>50%) due to pores that are less than 100 nm in diameter (see Figure 1). Unlike activated carbon powders, the carbon aerogels have high surface areas (ranging from 400-1000 m<sup>2</sup>/g) which are inherent to the sol-gel process and do not depend on "activation" procedures. A characterization of the primary particles that make up the aerogel network shows that they are composed of nanocrystalline, graphite-like ribbons that are intertwined to form the particles. Another very important distinction from other high surface area carbon powders is that carbon aerogels have oxygen free surfaces that can increase their effectiveness in some applications, particularly in the presence of NO<sub>2</sub> and SO<sub>2</sub> in a typical hot flue gas mixture. The gas/vapor adsorption method was used for determining this study's aerogel surface areas (silica aerogel: 980 m<sup>2</sup>/g and carbon aerogel: 750 m<sup>2</sup>/g).

#### Sample Preparation:

Aerogels are ideal for use in composites where the silica aerogel makes up the substrate and additional phases are added during sol-gel processing. This study used three different kinds of added materials into the silica sol-gel. The first test included spheres of preformed carbon aerogels. The second test involved a porous activated carbon (NORIT) and the third test uses a reducing gas to modify the aerogel composites formed in tests one and two. This procedure allows fabrication of chemically altered aerogel materials that also retain their structural integrity. The aerogel materials produced using this technique typically exhibit a variety of unique properties, such as enhanced chemical activity.

### **Experimental Setup and Discussion of Results**

#### Mercury adsorption test on aerogels:

Mercury in a flue-gas stream is present only in trace quantities (5-12 µg/m<sup>3</sup>) and this study focused on using 10 µg/m<sup>3</sup> at the inlet valve. The aerogel material was finely distributed on a silica filter and packed in a quartz-glass reactor (both have negligible surface areas compared with the aerogel). A mercury analyzer (Semtech 2000) was utilized to measure Hg<sup>0</sup>(g) on a continuous basis for up to three hours. The proportions of the different species, Hg<sup>0</sup>(g) and Hg<sup>2+</sup>X(g) in the IGCC system are not understood and, therefore, the experiments were repeated and total mercury at the outlet was monitored after passing the exiting gas over a SnCl<sub>2</sub> reducing unit (as was done successfully in related mercury studies<sup>6-7</sup>). Sorbent mass (for different aerogels) was set to range between 10-100 mg which is well beyond the range where mass transfer might be of concern, however, the pure aerogels have extremely low densities while the composites (aerogel plus active carbon) assume greater densities depending on the carbon loading ratios. A significant sorbent/mercury mass ratio of at least 1000/1 requires a minimum of 10 mg/m<sup>3</sup> of sorbent. The transport of mercury species to the aerogel's active surface sites was facilitated using a typical flue gas mixture (Table 1) containing ~ 7 % H<sub>2</sub>O vapor. Due to the elevated temperatures of the experiments (120-250 °C) the aerogels will not absorb any moisture. As the samples cool, however, the surfaces, which are covered with hydroxyl groups (~ 5 -OH/nm<sup>2</sup>) tend to exert strong hydrogen-bonding effects, causing the surfaces to act hygroscopic and handling procedures become more difficult. Although the aerogels's tendency to attract water can be eliminated through simple treatment with trimethylsilyl /or other non-polar aliphatic groups (-OR), this study preferred the presence of the polar acidic counter parts for the inorganic fraction of the aerogel composites.

Results of the mercury adsorption onto different aerogels are summarized in Table 2. In general, after a maximum of three hours of exposure time of the simulated hot flue gas (see flue-gas; Table 1), the chemically active silica aerogel (AERO-I), which had been pretreated with a reducing gas (H<sub>2</sub>), adsorbed 92 % of the total mercury (58 % after 30 minutes exposure). The aerogel composite utilizing the NORIT activated carbon product (AERO-II) adsorbed 43 % of the total mercury after 3 hours and less than a third of that amount after 30 minutes. Without the SnCl<sub>2</sub> reducing unit, only 17 % of Hg<sup>0</sup>(g) was detected after the maximum exposure time suggesting that the majority of the mercury was oxidized by the sorbent interaction. Without chemically activating the silica aerogel, the active carbon/aerogel composite functioned predominantly as a catalytic surface to oxidize the Hg<sup>0</sup>(g) (even without the presence of chlorine species to form the thermodynamically most stable form of Hg<sup>2+</sup>X(g)), but did not have excellent sorption capacity for the mercury as did the AERO-I. The third aerogel utilized in this study (AERO-III), which was also prepared as a composite, but incorporated a carbon aerogel rather than the activated NORIT, had good sorption capacity towards mercury, adsorbing 71 % of the total inlet mercury concentration after 3 hours (54 % after 30 min.). However, the overall capacity was somewhat less compared with the chemically active silica aerogel (AERO-I). This study suggests that the difference in oxygen concentration on the surfaces of the NORIT carbon and carbon aerogel may significantly influence the conversion reaction of Hg<sup>0</sup>(g) to Hg<sup>2+</sup>X(g) and the dominant species for chemisorption seems to be Hg<sup>0</sup>.

**Table 1** Flue-gas used in Hg tests

Carrier Flue Gas	% vol
H <sub>2</sub> O	7
SO <sub>2</sub>	1000ppm
NO <sub>2</sub> /NO	1000ppm
N <sub>2</sub>	Difference
CO <sub>2</sub>	12
O <sub>2</sub>	6
Hg	(10 µg/m <sup>3</sup> )

**Table 2** Results for Hg adsorption on aerogels\*

Sorbent Type	Hg adsorption	
	30 min	180 min
AERO-I	58 %	92 %
AERO-II	11 %	43 %
AERO-III	71 %	54 %

\* Table 2 shows mercury adsorption expressed as percent of the total Hg removed from the system after exposure time.

### *H<sub>2</sub>S(g) adsorption tests on aerogels*

The combination of in-situ desulfurization (50-60% desulfurization degree) and external desulfurization (completion until >90% sulfur capture) offers an attractive practical solution for hot sulfur abatement in IGCC systems. Work on the use of injected sorbents for in-situ gas desulfurization showed that for sorbent particles injected at high temperatures (1650°C), CaO for example preferably reacts with the silicate phase typically present in coal slag instead of the H<sub>2</sub>S present in the gas phase. Besides carbon based sorbents, various metal oxide sorbents, either ZnO-based or CuO-based, as well as mixed metal oxides (binary and tertiary combinations) have been compared in previous works.<sup>10</sup> In this study the H<sub>2</sub>S was carried to the aerogel sorbent using a carrier gas (Table 3) that had a composition similar to that typically present in a IGCC system after the majority of sulfur had already been pre-scrubbed (recovered as value-added products). The simulated gas was enriched with 1000 ppm H<sub>2</sub>S for the tests and the temperatures of the runs were fixed at 800 °C. Results are summarized in Table 4.

**Table 3** Carrier gas for H<sub>2</sub>S

Carrier gas	%vol
H <sub>2</sub>	30.5
CO	39.5
CO <sub>2</sub>	10.8 1
H <sub>2</sub> S	1000ppm
N <sub>2</sub>	Difference
H <sub>2</sub> O	1.5
T °C	800 °C

**Table 4** Results for H<sub>2</sub>S adsorption on aerogels

Sorbent type	H <sub>2</sub> S adsorption
AERO-I	NA
AERO-II	complete after 1 h
AERO-III	complete after 10 min.

The chemically activated silica aerogel (AERO-I) was not used for the H<sub>2</sub>S(g) adsorption tests. The aerogel composite with the NORIT carbon (AERO-II) had excellent adsorption capacity with all of the H<sub>2</sub>S(g) being captured after 1 hour exposure time. The carbon aerogel-composite (AERO-III) had much faster reaction rates compared with the NORIT carbon and complete H<sub>2</sub>S(g) capture was observed after only 10 minutes exposure time. Although both kinds of sorbents have excellent capacities, the mechanisms that control capture in the case of the carbon aerogel (AERO-III) are superior due to the rapid kinetics. To better understand the sorbent performance, experiments are required to further determine sorption rates as a function of reactor conditions.

The final experiment involved both mercury and H<sub>2</sub>S(g). The AERO-III that was first used to chemisorb H<sub>2</sub>S(g) was cooled to 200 °C and then a flue-gas enriched in 10 µg/m<sup>3</sup> mercury was passed over the sorbent. The H<sub>2</sub>S molecules which had chemisorbed onto the aerogel composite (this study was not able to tell whether the H<sub>2</sub>S molecules attached to the silica surfaces, or to the carbon surfaces, or both) reacted with the mercury to form HgS crystallites which can be seen in a high resolution SEM shown in Figure 2.

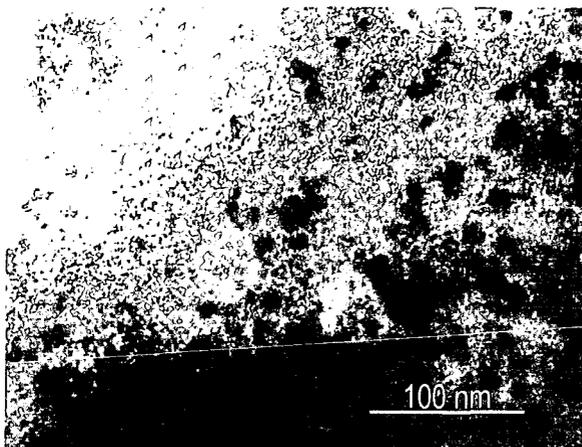


Figure 2 illustrates a high resolution SEM of the aerogel composite AERO-III after adsorption cycles involving first H<sub>2</sub>S sorption at 800 ° C and, after cooling to 200 ° C, a second adsorption cycle with a typical flue gas enriched in mercury was performed. The dark circles represent sites where Hg<sub>2</sub> nucleated and grew within the composite AERO-III.

#### Synopsis

Ideally, new IGCC technologies provide electricity while conforming to the strictest air-quality requirements and there is a driving force to find new and enhanced sorbents. Aerogel composites through sol-gel processing including silica and carbon based aerogels were shown to have excellent potential to adsorb both mercury and H<sub>2</sub>S(g) and future experimental work needs to focus on optimizing the conditions at which these sorbents could become economically feasible.

#### References

- 1 Graaf, J.M. van de, Bijl, E. van der, Stol, A, Kapteijn, F., Moulign, JA. (1998) Industrial and Engineering Chemistry Research, 37, p. 4071-4083.
- 2 Houghton, J.T., L.G. Meira Filho, J.P. Bruce, Hoesung Lee, B.T. Callander, E.F. Haites, N. Harris, and K. Maskell (1994). Cambridge University Press, Cambridge and New York, 339 pp.
- 3 U.S. Environmental Protection Agency. (1997) Office of Air Quality Planning and Standards and Office of Research and Development, EPA-452/R-97-003.
- 4 Laudal, D.L., Galbreath, K.C. and Zygarlicke, C.J. (1996) Fourth International Conference on Mercury as a Global Pollutant, Hamburg, Germany.
- 5 Galbreath, K.C and Zygarlicke, C.J. (1998) Conference Proceedings, Air Quality, Mercury, Trace Elements and Particulate Matter. McLeen, Virginia, p. 1-23 Galbreath
- 6 Miller, S.J. and Brown, T.D. (1998) Conference Proceedings, Air Quality, Mercury, Trace Elements and Particulate Matter. McLeen, Virginia, p. 1-23 Miller
- 7 Miller, S.J., Olson, E.S., Dunham, G.E. and Sharma, R.K. (1998) Air & Waste Management Association's 91<sup>st</sup> Annual Meeting & Exhibition, San Frandiego, CA, Paper 98-RA79B.07
- 8 Ghorishi, B. and Gullett, B.K (1997) Proceedings of the EPRI-DOE-EPA Combined Utility Air Pollutant Control Symposium; Washington, DC, Aug.25-29; EPRI TR--108683-V3.
- 9 Zhao, L.>, and Rochelle, G.T. (1998) Ind. Eng. Chem. Res., 37, P.380-387.
- 10 Aylett, B.J. 1975 Pergamon Texts in Inorganic Chemistry, Pergamon Press Ltd. Vol. 18.
- 11 Hunt, A.J., Ayers, M.R. and Cao (1995) Journal of Non-Crystalline Solids 189. P264-270.
- 12 Tewari, P.H., Lofftus, K.D., and Hunt, A.J. (1985) 2. Intemational conference on ultrastructure processing of ceramics, glasses and composites. Daytona Beach, FL. Lawrence Berkeley Lab, CA. pp.17
- 13 Hrubesh, L.W., and Pekala (1994) Journal of Material Research 9. P 731-738
- 14 Zeng, S.Q., Hunt, A.J., Cao, W. and Greif, R. (1994) Journal of Heat Transfer 116. P.756-759.
- 15 Hua, d.W., Anderson, J., Digeregorio, J., Smith, D.M., and Beaucage, G. (1995) Journal of Non-Crystalline Solids 186. 142-148.
- 16 Yokogawa, H. and Yokoyama, M. (1995) Journal of Non-Crystalline Solids. 186. 23-29.
- 17 Song, X.Y., Cao W.Q., Ayers, M.R., and Hunt, A.J. (1995) Journal of Materials Research 10. P. 251-254

## HOT GAS DESULFURIZATION WITH Z-SORB® SORBENTS

Gyanesh P. Khare and Gil J. Greenwood

Phillips Petroleum Company  
Downstream Research and Development  
Bartlesville, OK 74003

Keywords: Sorbent, Clean Coal, Coal Gasification, Fuel Gas, Desulfurization, Hydrogen Sulfide, IGCC, Regenerable Sorbent, Syngas, Zinc Oxide

### Introduction

Originally designed as a sorbent for tail gas cleanup [1], Phillips Z-Sorb® Sorbent has found application for the removal of hydrogen sulfide from the fuel gas that is generated in a clean coal process. For the latter technology, previous fixed bed sorbents have shown poor mechanical stability due to spalling when adsorbing hydrogen sulfide in reducing gas atmospheres or when being regenerated over many cycles [2].

Bench scale fixed-bed tests conducted at the Morgantown Energy Technology Center showed that Z-Sorb® sorbent performed better than zinc titanate [3,4]. The performance of the sorbent in a moving-bed application at General Electric was very encouraging [5]. The sorbent flowed well, H<sub>2</sub>S was reduced to less than 50 ppm at the absorber outlet over long periods and post-test analyses of the sorbent indicated very low sulfate levels at the regenerator exit. The fluidizable version of the novel sorbent was initially tested in Research Triangle Institute's high temperature, high pressure, semi-batch, fluidized-bed reactor system [6]. In a life cycle test consisting of 50 cycles of sulfidation and regeneration, this sorbent exhibited excellent activity and regenerability. The sulfur loading was observed to be 90+ percent of the theoretical capacity. The sorbent consistently demonstrated a sharp regeneration profile with no evidence of sulfate accumulation.

Tests with Z-Sorb® sorbents for desulfurization of coal derived gases were conducted at moderate pressure (507-2027 kPa) and a broad range of operating temperatures (315-540 °C). Earlier studies emphasized the upper end of this temperature range since it is proposed for most gasification projects [4, 7, 8]; other studies have shown the new sorbent formulations operate at lower temperatures (315-425 °C) [1, 4, 9]. These sorbents fulfill the requirements of long term sorbent reactivity, chemical/mechanical stability and attrition resistance.

This paper will provide a summary of the performance of Phillips proprietary Z-Sorb® sorbents at a number of test locations in the United States and Europe. Project participants working with Phillips in this study have been the M. W. Kellogg Company, General Electric (GE), Research Triangle Institute (RTI), Morgantown Energy Technology Center (METC) and members of the European Coal and Steel Community (ECSC).

### Sorbent Characteristics

A sorbent for hot gas desulfurization must demonstrate high chemical reactivity, as measured by the rate of sulfur absorption and the sulfur loading capacity, and physical integrity. In addition, for fluidized-bed/transport reactor operation the sorbent must also have good fluidizing characteristics and mechanical strength characterized by low attrition losses. Phillips Petroleum Company has developed suitable sorbent for each of the reactor types currently being developed for the hot gas desulfurization technology. Extruded, spherical, and granular Phillips sorbent formulations are now available for fixed-bed, moving-bed, and fluidized-bed/transport reactor systems, respectively. For fixed-bed reactor the sorbent used was in an extruded form consisting of 1/8" pellets having a bulk density of about 1.0 g/cc. A fluidized version of Phillips' sorbent had an average particle size of 175 micron, a particle size range of 50-300 micron and an apparent bulk density of 0.90-1.00 g/cc. For a moving-bed reactor, a spherical sorbent with an average pellet diameter of 4.1 mm and bulk density of 0.96 g/cc was used.

### Bench/Pilot Scale Testing

Phillips Petroleum Company has conducted extensive testing of its proprietary Z-Sorb® sorbent with several research partners in the United States and Europe. Table I summarizes the important parameters from each of these tests. The data reveals a number of facts. It is evident that this sorbent has a high chemical reactivity for sulfur capture. Generally, a sulfur loading of 15-20 wt% is easily achieved. The most striking feature of this sorbent was its high efficiency for sulfur removal with a very sharp breakthrough. Removal of sulfur in various fuel gases to less than 10 ppm under most conditions and perhaps close to zero ppm under some conditions has been demonstrated [4, 10-15]. The data presented in Table I also show that sulfur removal ability of this sorbent is totally unaffected by the gas

composition. The sorbent appears to be effective in removing sulfur from a broad composition range of fuel gases produced by different types of gasifiers ranging from KRW to Shell.

The application of Z-Sorb® sorbent in removing sulfur from authentic gasifier product gases generated from biofuel/brown-coal was investigated by TPS Termiska Processor AB (Sweden). Of the various commercially available sorbent tested, this study found Z-Sorb® sorbent to be the most promising. The sorbent reduced the sulfur content in the effluent stream to below 10 ppm and fully reactivated after desorption at steam concentrations up to 15% at pressures up to 20 bar. Z-Sorb® sorbent was also less sensitive to steam concentration than a zinc titanate sorbent, ZT-4 [ 11 ].

Recent work with modified formulations suggests the sorbent temperature application range can be expanded to include the lower temperatures (260-430 °C) used for moderate temperature gas cleanup. Our research found that zinc oxide-based sorbents are effective in desulfurization above 315 °C. Even at temperatures of 315-430 °C the sulfur capacity retained forty to fifty percent of a typical value obtained at higher temperatures, such as 540°C. Figure 1 gives the bench scale test results for the temperature dependence of the sulfur loading capacity of Z-Sorb® sorbent. These runs were done at atmospheric pressure with 4.2% H<sub>2</sub>S in CO<sub>2</sub>/N<sub>2</sub> and a gas hourly space velocity of 1440 h<sup>-1</sup>. The sorbent was a fluid bed material. Sulfur loadings of 6-22 wt% in the temperature range of 315-650 °C are quite suitable for a variety of processes currently under development in the Integrated Gasification Combined Cycle (IGCC) program. We also have Thermogravimetric Analysis (TGA) reactivity data that amplify these results. Figure 2 presents the chemical reactivity of a fresh sorbent exposed to simulated coal gases at different temperatures. There is a slight fall-off in sulfur loading as the temperature of absorption is reduced from 540 °C to 370 °C, but the rate at which hydrogen sulfide is absorbed does not suffer as much.

In the long-term bench testing at Phillips Petroleum, the sulfur loading capacity of Z-Sorb® sorbent was found to remain high over a large number of cycles. Figure 3 shows the remarkable performance of an extruded, fixed-bed formulation at an absorption temperature of 430 °C. For nearly 700 cycles of absorption and regeneration, the loadings remain at a high level, starting at 14% and ending at 8%. For most of the cycles, the sorbent picked up at least 10% sulfur, which is 50% of the theoretical loading.

### Problem of Sulfate Formation

One of the major concerns in developing regenerable sorbent is formation and accumulation of sulfates in the sorbent during multi-cycle use. Accumulation of sulfates is not desirable as it not only affects the sulfur removal efficiency of the sorbent, but in some cases, for example in zinc titanate sorbents, it has been shown to cause spalling of pellets resulting in fatal failures during process. Although, this problem is not prevalent in Z-Sorb® sorbents as the total sulfur content in the regenerated samples is normally less than 0.5 weight percent, we investigated the regeneration step in detail to examine conditions for the formation of sulfates. Thermogravimetric analysis was used to investigate the regeneration kinetics of a single pellet of sulfided Z-Sorb® sorbent and corresponding x-ray photoelectron spectroscopy (XPS) analysis of the regenerated pellet was performed. A sulfided sample was used for this analysis. It had about ten weight percent sulfur on it. As drawn in Figure 4, the weight loss curves for a single pellet regenerated at different temperatures from 480 °C to 755 °C indicate that 480 °C and 540 °C are ineffective in completely regenerating the sulfided absorbent. In fact, the sample at 480 °C gained weight. XPS measurements in Figure 5 agree on this point. The binding energy data of sulfur from XPS reveal a large amount of sulfide sulfur and sulfate sulfur on the sample after regeneration at 480 °C. Apparently, zinc sulfide converted to zinc sulfate, thereby increasing the weight of the sample. The 540 °C sample showed lower sulfide and sulfate sulfur, but there still was sufficient sulfide to show that regeneration was incomplete. By 565 °C, there was no sulfide left, and by 755 °C, there was no sulfate left. This finding is in agreement with the decomposition temperature of zinc sulfate, which is 740 °C [15].

### Bibliography

1. **Brinkmeyer, F. M., and G. A. Delzer**, " Z-Sorb®-A New Sulfur Removal Process", AIChE National Meeting, San Diego, CA, August (1990).
2. **Mei, J. S., L. D. Gasper-Galvin, C. E. Everitt, and S. Katta**, "Fixed Bed Testing of a Molybdenum-Promoted Zinc Titanate Sorbent for Hot Gas Desulfurization", Proceedings of the Coal-Fired Power Systems 93-Advances in IGCC and PFBE Review Meeting, DOE/METC-93/6131, NTIS/DE 93000289, Springfield, VA (1993).
3. **Campbell, W. M., J. J. O'Donnell, S. Katta, T. Grindley, G. Delzer, and G. P. Khare**, "Desulfurization of Hot Fuel Gas with Z-Sorb® III Sorbent", Proceedings of the Coal-Fired Power Systems 93-Advances in IGCC and PFBC Review Meeting, DOE/MET-93/6131, NTIS/DE 9300289, Springfield, VA (1993).
4. **Delzer, G.A., G. P. Khare, and G. J. Greenwood**, (1993). "Z-Sorb® Absorbent for Hot

- Gas Desulfurization", AIChE Annual Meeting, Symposium on Gas Purification, No. 130f, St. Louis, MO., November 7-12.
5. **Gal, E., D. Najewicz, A. H. Furnam, R. Ayala, and A. Feitelberg**, "Integrated Operation of a Pressurized Gasifier, Hot Gas Desulfurization System and Turbine Simulator", Fourteenth Annual Gasification and Gas Stream Cleanup Systems Contractors Review Meeting, Morgantown, WV, June (1994).
  6. **Gupta, R. P., and S. K. Gangwal**, "Enhanced Durability of Desulfurization Sorbents for Fluidized-Bed Applications—Development and Testing of Zinc Titanate Sorbents", Topical Report to DOE/MC/25006-3271. Morgantown Energy Technology Center, U.S. Department of Energy, Morgantown, WV. November (1992).
  7. **Khare, G. P., G. A. Delzer, D. H. Kubicek, and G. J. Greenwood**, (1994). "Hot Gas Desulfurization with Phillips Zinc Based Sorbents", AIChE Annual Meeting, Symposium on Gas Purification, No. 247e, San Francisco, CA, November 13-18.
  8. **Khare, G. P., G. A. Delzer, D. H. Kubicek, and G. J. Greenwood** (1995). "Hot Gas Desulfurization with Phillips Sorbent in Moving-Bed and Fluidized-Bed Reactors", *Environmental Progress*, Vol. 14, pp. 146-150.
  9. **Khare, G. P., G. J. Greenwood, D. H. Kubicek and G. A. Delzer**, (1995). "Regenerable Sorbents for Low Temperature Desulfurization of Coal Gas", Proceedings of the 12th Annual Pittsburgh Coal Conference, p. 1080, Pittsburgh, PA, September 11-15.
  10. **Fantom, I. R. and S. Radford**, "Performance of Regenerable Sulfur Sorbents on Coal Derived Fuel Gas", High Temperature Gas Cleaning, Ed. by E. Schmidt...-1<sup>st</sup> Ed.-Karlsruhe Institute für Mechanische und Mechanik, 1996.
  11. **Hagstrom, P. and A. Hallgren**, "Bromass for Energy and Industry", 10th European Conference and Technology Exhibition, Wurzburg, Germany, June 8, 1998.
  12. **Bevan, S, D. Najecwicz, E. Gal, A. H. Furman, R. Ayala and A. Feitelberg**, (1994). "Integrated Operation of a Pressurized Gasifier", Hot Gas Desulfurization System and Turbine Simulator, In Proceedings of the Coal-Fired Power Systems 94—Advances in IGCC and PFBC Review meeting. p. 222, DOE/METC94/1008 NTIS/DE 94012252, Springfield, VA: National Technical Service.
  13. **R. P Gupta, S. K. Gangwal and G. P Khare**, (1994). "Fluidized-Bed Testing of Z-Sorb III Sorbent", Topical Report to DOE/METC. Contract No. DE-AC21-88MC 25006, May.
  14. European Coal and Steel Community, Annual Meeting, June 1994. Cheltenham, England. Private communication.
  15. **H. R. Perry and C. H. Chilton**, 1973 Chemical Engineers' Handbook, 5th Edition, McGraw-Hill, New York, p.3-24.

Table 1. Z-Sorb® Sorbent Testing Summary for Hot Gas Cleanup

Research Partner	Process Type	Test Scale	Operating Temperature (C)	Operating Pressure (kPa)	Regeneration Temperature (C)	Coal Gas	Sulfur Loading (gS/100g Sorbent)	Effluent Sulfur (ppm)	Ref.
DOE Morgantown	Fixed Bed	Laboratory	538	1038	482-732	Simulated KRW	14	0	4
CTDD of British Coal	Fixed Bed	Pilot Plant	540	1051	540-750	Air-Blown Gasifier	10.5	<10	10
CIEMAT	Fixed Bed	Pilot Plant	400	1050-2027	550	Simulated EcoGas	15.4-16.9	<20	
TPS	Fixed Bed	Laboratory	490	1050-2027	550	Black&Brown Coal	not det.	4.7	11
General Electric	Moving Bed	Laboratory, Pilot Plant	538	2027	730	Lurgi Gasifier		<50	12
Research Triangle Institute	Fluid Bed	Laboratory	538	2027	590-790	Simulated U-Gas	10.0-20.2	10	13
CTDD of British Coal	Fluid Bed	Pilot Plant	520-540	1051	575-717	Airblown Gasifier	13-15	<10	10
Research Laboratory A	Fluid Bed	Laboratory	400	2027	600	Shell Type	17.5-20.3	<1	14
M W Kellogg	Fluid Bed	Pilot Plant	538-555	690	538	1% H <sub>2</sub> S in H <sub>2</sub>	15.4	0	18

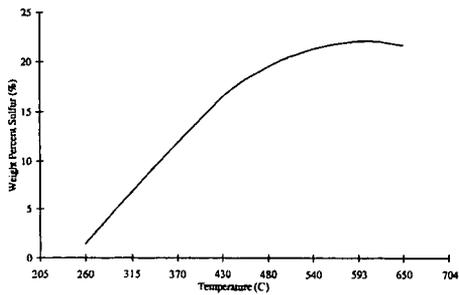


Figure 1. Sulfur Loading Capacity as a Function of Temperature

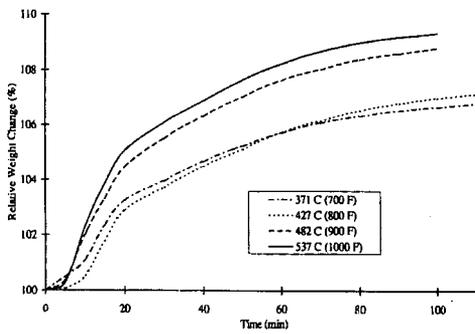


Figure 2. TGA Sulfur Loading Capacity

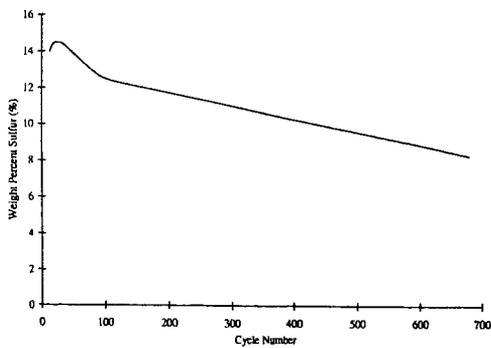


Figure 3. Sulfur Loading Capacity as a Function of Cycle

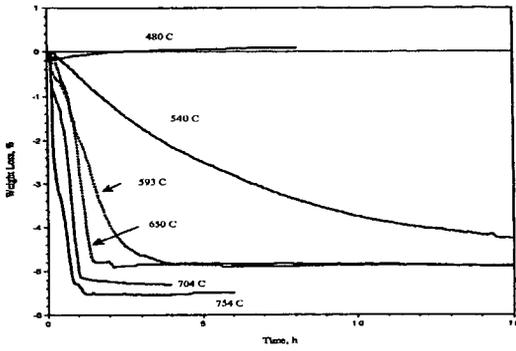


Figure 4. TGA Analysis for Sulfided Z-Sorb® Sorbent

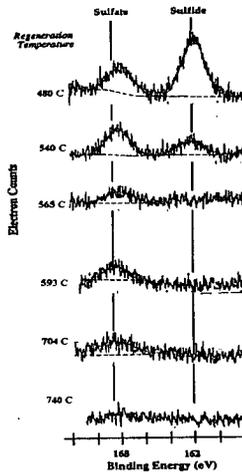


Figure 5. Z-Sorb® Sorbent XPS Analysis of Regenerated Samples

# EXPERIMENTAL STUDY ON THE FLAME STABILITY AND THE NO<sub>x</sub> EMISSION CHARACTERISTICS OF LOW CALORIFIC VALUE COAL DERIVED GAS FUEL USING FLAT FLAME BURNER

**Chan Lee and Yong Chul Kim**

Department of Mechanical Engineering, University of Suwon  
Suwon PO Box 77, Suwon, Kyunggi-Do, Korea, 445-743

**Hyung Taek Kim**

Department of Energy Studies, Ajou University  
Wonchon-Dong, San-5, Paldal-Gu, Suwon, Korea, 442-749

**Key Words:** Coal Derived Gas, Flame Stability, Fuel NO<sub>x</sub>

## ABSTRACT

Experimental studies are conducted to investigate the flame stability and the thermal/fuel NO<sub>x</sub> formation characteristics of the low calorific value (LCV) coal derived gas fuel. Synthetic LCV fuel gas is produced by mixing carbon monoxide, hydrogen, nitrogen and ammonia on the basis that the thermal input of the syngas fuel into a burner is identical to that of natural gas. The syngas mixture is fed to and burnt with air on flat flame burner. With the variation of the equivalence ratio for specific syngas fuel, flame behaviors are observed to identify the flame instability due to blow-off or flashback and to define stable combustion range. Measurements of NO<sub>x</sub> content in combustion gas are made for comparing thermal and fuel NO<sub>x</sub> from the LCV syngas combustion with those of the natural gas one. In addition, the nitrogen dilution of the LCV syngas is preliminarily attempted as a NO<sub>x</sub> reduction technique, and its effects on thermal and fuel NO<sub>x</sub> production are discussed.

## INTRODUCTION

Integrated Gasification Combined Cycle(IGCC) is emerging as a next-generation coal-based power plant because of its low fuel cost, competitive capital cost, high thermal efficiency and superior environmental performance. However, the gas fuel for gas turbine combustion in IGCC power plant is produced through oxygen-blown coal gasification and gas clean-up processes, so it is composed mainly of hydrogen, carbon monoxide and nitrogen that result in low calorific value of the fuel, 1/4-1/5 times smaller than the natural gas. In addition, due to high content of hydrogen in fuel, the LCV coal derived

gas shows very fast burning velocity, chemical reaction rate and high flame temperature[1]. As the consequence, flame instability can hardly be avoided in premixed combustion and NO<sub>x</sub> formation rate becomes much higher than in the natural gas case. For this reason, the most of combustion tests for LCV coal derived gas are conducted on the diffusion type burners incorporating with nitrogen and/or steam dilution for NO<sub>x</sub> control[2,3] while premix burner technology being at the first stage of development.

Therefore, for the efficient premixed combustor in IGCC power plant, fundamental characteristics of combustion stability and NO<sub>x</sub> emission of the LCV fuel gas need to be investigated and would be useful in providing engineering guidelines for future R&D of IGCC gas turbine combustor. In the present experimental study, coal gas burner system is constructed with the flexibility in varying various fuel composition and equivalence ratio conditions, and flame behavior and stability of the coal gas are observed and furthermore thermal and fuel NO<sub>x</sub> emission values are measured.

## EXPERIMENTAL RESULTS AND DISCUSSIONS

As shown in Fig.1, experimental apparatus is composed of fuel/air feeding , premix burner and gas sampling/analysis systems. LCV fuel gas is simulated as synthetic gas that is produced by mixing carbon monoxide, hydrogen, nitrogen and ammonia. The syngas is premixed with air, fed to and burnt on flat flame burner with porous bronze water-cooled plate to produce uniform velocity distribution, and the burner does not employ the annular stream of inert gas as depicted in Fig.2. Flame behavior picture is recorded by using CCD/digital camera and image processing unit, and the NO<sub>x</sub> emission of sampled exhaust gas is analyzed.

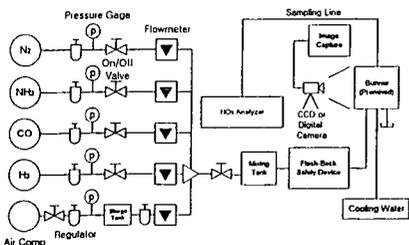


Fig.1 Schematic Diagram of Experimental Apparatus

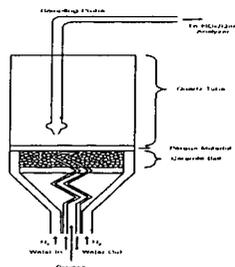


Fig.2 Flat Flame Burner

Before syngas combustion test, a reference experiment is carried out with natural gas fuel of the constant flow rate at 0.48 LPM. Flame of natural gas remains stable within the equivalence ratio range from 0.6 to 1.3, and its NO<sub>x</sub> emission level shows lower than 50 ppm. Syngas fuel is produced by mixing carbon monoxide and hydrogen to match the composition of actual coal gas fuel derived from oxygen blown gasifier, CO: 70-90 % and H<sub>2</sub>: 10-30% on volume basis. Fuel flow rate is determined on the basis

that the thermal input of the syngas fuel is identical to that of natural gas. In addition, the present study considers  $\text{NH}_3$  of 0-3000 ppm in syngas fuel to investigate the effect of  $\text{NH}_3$  on fuel  $\text{NO}_x$  formation. Table 1 represents the fuel flow rates and the compositions of three different syngas fuels used in the present study.

Table 1 Composition and Flow Rate of Syngas Fuel

Syngas No.	$\text{CO}(\%)$	$\text{H}_2(\%)$	$\text{H}_2/\text{CO}(\%)$	Flow Rate(LPM)
1	91.0	9.0	9.9	1.64
2	82.0	18.0	34.1	1.66
3	70.0	30.0 </td <td>42.8</td> <td>1.69</td>	42.8	1.69

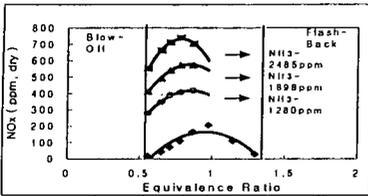


Fig.3(a)  $\text{NO}_x$  & Flame Stability of Syngas #1

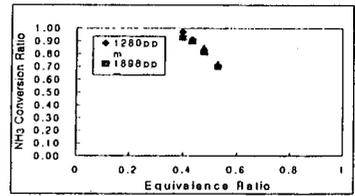


Fig.3(b)  $\text{NH}_3$  Conversion Ratio of Syngas #1

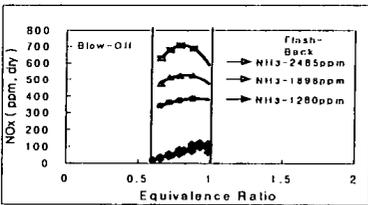


Fig.4(a)  $\text{NO}_x$  & Flame Stability of Syngas #2

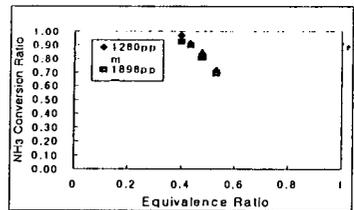


Fig.4(b)  $\text{NH}_3$  Conversion Ratio of Syngas #2

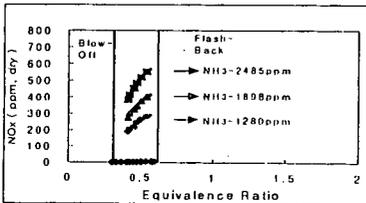


Fig.5(a)  $\text{NO}_x$  & Flame Stability of Syngas #3

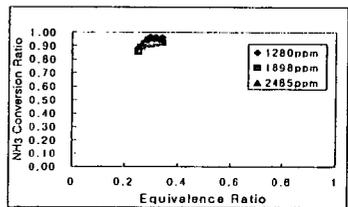


Fig.5(b)  $\text{NH}_3$  Conversion Ratio of Syngas #3

Figs. 3(a), 4(a) and 5(a) illustrate the flame stability range and the NO<sub>x</sub> emission of syngases with H<sub>2</sub>/CO= 9.9, 34.1 and 42.8 % respectively. They show that the flame stability range of syngas is shrunken into narrower range at higher H<sub>2</sub>/CO ratio. These experimental results can be explained by that flashback occurs at lower equivalence ratio point due to higher burning velocity with the increase of H<sub>2</sub>/CO ratio of syngas[4]. It is deduced from the measured results that if coal gas firing gas turbine combustor is designed with the same burner as the natural gas case, it can be operated only at narrow combustion condition range so careful design modification must be made on air distribution in combustor. As shown also in Figs. 3(a),4(a) and 5(a), thermal NO<sub>x</sub> emission level is lowered for higher H<sub>2</sub>/CO ratio syngas fuel with lower flame temperature at the stable combustion range. With the addition of NH<sub>3</sub>, NO<sub>x</sub> emission is more produced by the order of 200-300 ppm, compared with the cases of NH<sub>3</sub>, over entire combustion range and its peak point is shifted to lower equivalence ratio compared with the thermal NO<sub>x</sub>. Figs. 3(b), 4(b) and 5(b) present the variation of ammonia to NO<sub>x</sub> conversion ratio with equivalence ratio at three syngas fuel conditions, and they show ammonia is more easily converted to NO<sub>x</sub> at lower equivalence ratio condition[5,6].

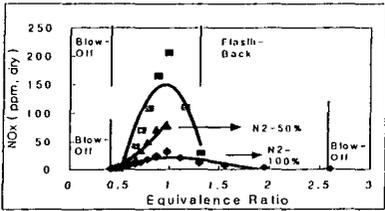


Fig.6 Effect of Nitrogen Dilution (Syngas#1)

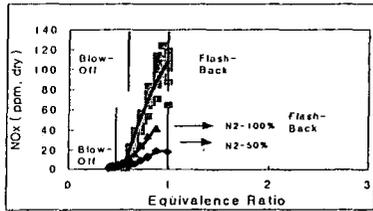


Fig.7 Effect of Nitrogen Dilution (Syngas#2)

The effects of nitrogen dilution on NO<sub>x</sub> reduction are examined in Figs. 6 and 7. The present study employs nitrogen diluent that is blended with syngas fuel before entering burner, and its amount is considered as 50 or 100% of fuel flow rate on volume basis. Nitrogen dilution results in remarkable NO<sub>x</sub> reduction as well as widening of flame stability range.

## CONCLUSIONS

Flat flame burner tests are conducted for investigating flame stability and NO<sub>x</sub> emission characteristics of three LCV syngas fuels with the same thermal input as the natural gas case. Flame stability range is shortened to narrower band of equivalence ratio and thermal NO<sub>x</sub> is less produced when burning the syngas with higher H<sub>2</sub>/CO ratio. The NH<sub>3</sub> content in fuel results in additional 200-300 ppm fuel NO<sub>x</sub> formation as well as the shift of peak NO<sub>x</sub> point to the lower equivalence ratio compared with the thermal NO<sub>x</sub> case. The conversion ratio of NH<sub>3</sub> to NO<sub>x</sub> ranges from 97 to 62% with the increase of equivalence

ratio. The effect of nitrogen dilution is very favorable both in reducing NOx emission and widening flame stability range.

## ACKNOWLEDGEMENT

This work was performed by the financial support of R&D Management Center for Energy and Resources(RaCER) in Korea.

## REFERENCES

1. K.Dobbeling et al., "Low-NOx Premixed Combustion of Btu Fuels Using the ABB Double Cone Burner(EV Burner)," ASME Journal of Engineering for Gas Turbines and Power, vol.118, pp.46-53, 1996
2. C.S.Cook et al., "System Evaluation and LBTU Fuel Combustion Studies for IGCC Power Generations," ASME Journal of Engineering for Gas Turbines and Power, vol.117, pp.673-677, 1995
3. B.Becker and B.Schetter, "Gas Turbine Above 150MW for Integrated Coal Gasification Combined Cycles(IGCC)," ASME Journal of Engineering for Gas Turbines and Power, vol.114, pp.660-664, 1992
4. T.G.Scholte and P.B.Vaags, "Burning Velocity of Mixtures of Hydrogen, Carbon Monoxide and Methane with Air," Combustion & Flame, vol.3, pp.511-524, 1959
5. T,Nakata et al., "A Study on Low NOx Combustion in LBG-Fueled 1500 °C-Class Gas Turbine," ASME Journal of Engineering for Gas Turbines and Power, vol.118, pp.534-540, 1996
6. R.P. Lindstedt and M.A.Selim, "Reduced Reaction Mechanism for Ammonia Oxidation in Premixed Laminar Flames," Combustion Science & Technology, vol.99, pp.277-298, 1994

# A STUDY ON THE SLAGGING BEHAVIOR OF COAL ASH IN GASIFICATION/COMBUSTION ENVIRONMENT USING DTF

Hyung-Taek Kim and Byung-Chul Choi

Energy Department, Ajou University

San 5, Wonchun-dong, Paldal-gu, Suwon, Korea, 442-749

Sang-Hwan Park

Materials Science & Technology Division

Korea Institute of Science & Technology

**Keywords:** coal ash, slagging, gasification

## ABSTRACT

The purpose of this study is to determine ash slagging behavior for the optimum ash removal in actual coal gasifier as well as combustor. DTF (drop tube furnace) was utilized for entire experiment to simulate real time and temperature history of coal particle. Pulverized particles of three different coal samples (Alaska, Cyprus and Datong) were injected into DTF with different experimental conditions. The slag samples deposited at the top of sample collector by the particle action of impacting and agglomerating. The formation shape of each deposited slag is related with physical properties of original ash such as ash fusion temperature, viscosity and surface tension. Phase diagram of main components of ash, i.e.,  $\text{SiO}_2\text{-CaO-Al}_2\text{O}_3$  system are analyzed to determine ash fusion behavior with different composition of the system. Shape of slag formation represents different behavior with gasification and combustion environment and also is effected by chemical composition of coal ash.

## 1. INTRODUCTION

Among the second-generation coal-fired power systems, IGCC (integrated gasification combined cycle) is characterized by highly efficient and environmentally sustainable technology. Since most of organic impurities of coal are converted into gas phase in gasification S- and N-containing gases can be easily separated from the product gas comparing to p.c. combustion technology. Moreover,  $\text{CO}_2$  emission is reduced in IGCC technology because of its high electricity efficiency. Inorganic impurities of coal are also converted into slag in slagging-type coal gasifier. The volume of coal slag is reduced to 1/2~1/3 and the heavy metal compounds in coal ash is vitrified to non-leaching glass form.

In this experimental investigation, DTF is utilized to determine the characteristics and formation phenomena of ash slag generated with different coal samples. The result is analyzed for the relationship with chemical composition, ash fusion temperature and fluidity properties of coal ash. With above information, actual behavior of coal ash inside gasifier/combustor can be predicted so that optimum-operating condition for smooth slagging can be suggested.

## 2. EXPERIMENT

Characteristics of slag produced in slagging-type gasifier play a major factor in the continuous operation of actual gasifier. Flow properties of slag usually depend on viscosity and melting temperature, which were varied with inorganic constituents of coal ash. Ashes of three coal samples are analyzed with ICP-AAS for the inorganic constituents and the results are shown in Table 1. Generally speaking, reducing agents such as  $\text{Fe}_2\text{O}_3$ , CaO and  $\text{Na}_2\text{O}$  behave a role in reducing viscosity and melting temperature. On the other hand, oxidizing agents such as SiO and  $\text{Al}_2\text{O}_3$  will increase viscosity and melting temperature.

Table 1. Chemical composition of coal ash samples

Composition(%)	SiO <sub>2</sub>	CaO	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	MgO
Datong	54.12	8.08	15.73	13.15	0.83	1.15	0.77	2.18
Alaska	44.83	20.20	19.30	7.01	1.11	0.70	1.40	3.90
Cypurus	51.60	11.37	19.30	5.73	0.84	2.71	0.83	2.11

Gas flow in the DTF reactor was arranged to laminar flow for the exact determination of reactivity and residence time of coal particles. The schematic diagram of DTF was shown in Fig. 1.

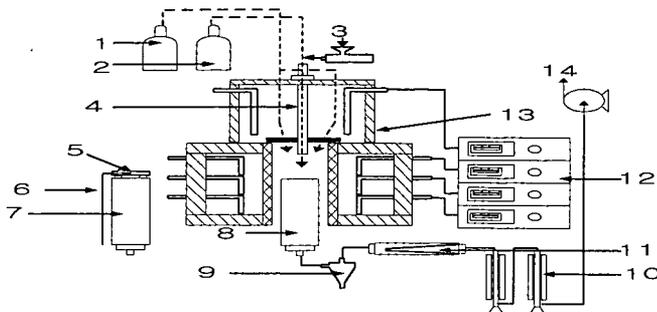


Fig. 1. Schematic diagram of Drop Tube Furnace (1: secondary gas line, 2: primary gas line, 3: coal feeder, 4: injector probe, 5: deposit disk, 6: R-type thermocouple, 7: deposit probe, 8: ash probe, 9: cyclone, 10: condenser, 11: ceramic filter, 12: PID controller, 13: furnace, 14: vent )

Coal feeding rate was fixed at 0.3g/min for entire experiment. In the combustion experiment, air were used for both primary and secondary carrier gas with the oxygen/coal weight ratio of 1.5. However, in the gasification experiment, primary gas was oxygen and secondary gas nitrogen with oxygen/coal ratio of 0.72, which is selected for maximum CO concentration in the product gas. While feeding coal particles at the top of the DTF and flowing carrier gases, reacted coal particles are collected at the top of deposit probe. Solid sample collector was installed inside deposit probe, which was made of metal substrate. Temperature was changed from 500°C to 600°C for the simulation of heat transfer surface. To investigate the reaction between coal ash and alumina refractory, solid sample collector was also made of alumina refractory that was installed at 1500°C in the deposit probe. Deposited ash samples was analyzed with photography for the shape of slag formation.

Ash fusion temperature was measured by standard ASTM method by using Ash Fusion Determinator (LECO model AF 600). Difference in FT and IDT, i.e.  $\Delta T$  is a factor which shows strength of ash deposit. Generally, if  $\Delta T$  is small, deposit thickness on reactor surface is thin and adhesive so that removal of ash deposit is very difficult. Table 2 shows fusion temperatures of each coal samples investigated in this study.

Table 2. Fusion Temperature of coal ash samples using ASTM method

Sample Coals	IDT(°C)	ST(°C)	HT(°C)	FT(°C)
Datong	1296	1304	1328	1359
Alaska	1205	1244	1263	1299
Cypurus	1249	1276	1301	1359

### 3. RESULTS AND DICUSSION

Liquid phase of coal slag behaves Newtonian fluid when flowing. When liquid phase is cooled, coal slag is transformed into pseudo-plastic solid state before solidification. Separation of solid state is dependent on composition of slag and transition temperature between liquid phase and solid phase, which is called critical viscosity temperature ( $T_{CV}$ ).  $T_{CV}$  has same meaning of slag removal temperature which is ASTM fusion temperature with maximum viscosity for smooth slag removal. Slag removal temperature was identified as

temperature with viscosity of 250 poise ( $T_{250}$ ) so that choice of suitable coal for slagging operation is mainly decided by the value of  $T_{250}$ . A value of  $T_{250}$  was decreased by increasing the amount of reducing agents and by decreasing the amount of oxidizing agents in coal ash. When viscosity of perfect liquid phase is determined, critical viscosity temperature ( $T_{CV}$ ) can be represented as crystallization temperature. Therefore  $T_{CV}$  and  $T_{250}$  have below relationship:  $T_{CV} > T_{250}$ , Slag removal temperature =  $T_{250}$ ,  $T_{CV} < T_{250}$ , Slag removal temperature =  $T_{CV}$ .

Variation of slag viscosity with different composition was calculated by Urbain equation that is based on  $CaO-Al_2O_3-SiO_2$  ternary phase diagram as in Frankel equation (1).

$$\ln \eta = A \exp(B/T) \dots \dots \dots (1)$$

When calculating slag viscosity for low rank coal, equation (2) is used, where T is temperature, A and B are function of chemical composition on coal ash,  $\eta$  is viscosity in poise and  $\Delta$  is silica percentage in slag.

$$\ln \eta = \ln A + \ln T + 10^3(B/T) - \Delta \dots \dots \dots (2)$$

When using this equation, proper classification of silica quantity is very important which is largely dependent on the B values. Calculated data of viscosity at the temperature of  $T_{CV}$  for each coal samples are illustrated in Table 3.

Table 3.  $T_{CV}$  and viscosity of ash sample

Sample Coals	Viscosity (poise)	$T_{cv}$ (°C)
Datong	348.18	1421
Alaska	364.92	1356
Cypurus	560.71	1394

The shape of slag samples with different experimental condition is illustrated in Fig. 2. Each formed slag shows slightly different shape with the variation of coal types and reaction atmosphere. Cypurus slag was not great difference between combustion and gasification condition, but shape of gasification slag more spherical shape than combustion condition. Datong slag shaped trigonal pyramid form and melting is started at the top of the deposit. Alaska slag shows flat melting shape because of its low melting characteristics. The variation of slag shape with different coal samples can be explained with the data of ash fusion temperature, surface tension and viscosity of slag with different slag composition. Also reactivity with refractory alumina substrate of solid sample collector affects shape of slag.

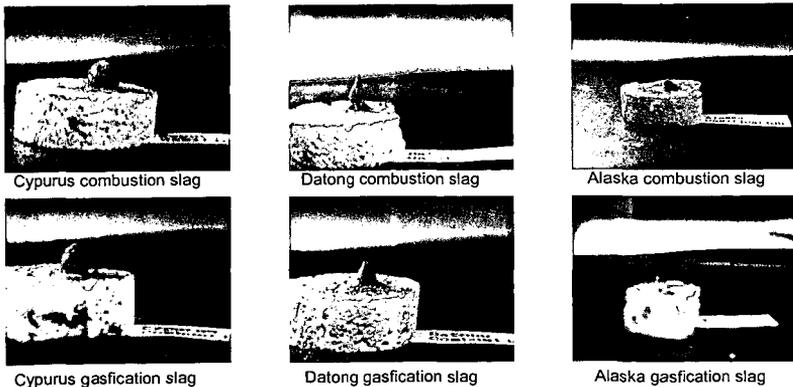


Figure. 2 Shape of ash slag with gasification/combustion condition and coal types

Coal samples in this study are classified into Alaska and Cypurus coal, which mainly consist of  $SiO_2-CaO-Al_2O_3$  phase and Datong coal, which mainly consist of  $CaO-SiO_2-Al_2O_3-Fe_2O_3$  phase. Mole fractions of  $Al_2O_3$  and  $Fe_2O_3$  in Alaska and Cypurus coals are constant but  $SiO_2/CaO$  ratio in ash components was varied from 2.07 in Alaska to 3.51 in Cypurus. For the slag samples mainly composed of  $SiO_2-CaO-Al_2O_3$ , viscosity is increased with increasing quantity of  $SiO_2$  in slag.

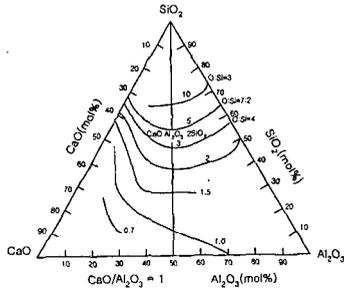


Figure 3. CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> ternary diagram for coal ash samples

As shown in Fig. 3, however, Datong slag, composed of high quantity of SiO<sub>2</sub> and low CaO, would expected low fusion temperature and low slag viscosity. The main reason of such finding is because the reaction between high quantity of Fe<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> formed Fayalite(Fe<sub>2</sub>SiO<sub>4</sub>) which has low fusion temperature. Such finding is probably based on the fact that increasing quantity of Fe<sub>2</sub>O<sub>3</sub> destroyed network structure of SiO<sub>2</sub>. Shape of slag formation with different gasification/combustion condition was effected by chemical composition of coal ash.

However, shape of slag drop was mainly determined by surface tension value, which is subjected to wetting angle. Wetting angle between alumina refractory substrate and melting slag was represented by Young's relation as in equation (3), where O is wetting angle, r<sub>sv</sub>, r<sub>sl</sub> and r<sub>lv</sub> are surface tension of solid-vapor, solid-liquid and liquid-vapor.

$$\cos O = (r_{sl} - r_{sv})/r_{lv} \text{-----(3)}$$

If surface tensions of solid-vapor and solid-liquid are constant, surface tension of liquid-vapor phase behave major factor in the formation of slag drop. In other words decreasing surface tension of melting slag increase wetting angle. As a result, non-wetting surface was formed so that formed slag is not penetrated into porous alumina substrate.

#### 4. CONCLUSION

To determine optimum operation condition of ash slagging in coal gasifier/combustor, DTF is utilized, which can simulate time and temperature history of coal particle. Slagging behavior of coal ash samples was also investigated with empirical equations and the results showed that slagging behaviors of subbituminous Alaska and Datong coals were much better than Cypurus. Separation of solid state dependant on composition of slag and transition temperature between liquid phase and solid phase by experiment data. Shape of slag formation with different on gasification/combustion condition was effected by chemical composition of coal ash. Shape of slag drop was determined by surface tension value, which is subject to wetting angle.

#### ACKNOWLEDGEMENT

This work was performed by the financial support of R&D Management Center for Energy and Resources (RaCER) in Korea.

#### REFERENCE

1. S. K. Gupta et al., " Ash Fusion Temperatures and the Transformations of coal ash particles to slag," Fuel Processing Technology, vol.56, pp.33-43, 1998
2. H. B. Vuthaluru et al., " Ash Formation and Deposition from a Victorian brown coal-modeling and prevention," Fuel Processing Technology, vol.53, pp.215-233, 1998
3. J. N. Harb et al., " Use of Equilibrium Calculations To Predict the Behavior of Coal Ash in Combustion Systems," Energy & Fuels, vol.7, pp.208-214, 1993
4. Inorganic Transformations and Ash Deposition during Combustion, edited by S. A. Benson, The American Society of Mechanical Engineers, pp.121-131, 1991