

## **4.2 Beneficiation of Low-Rank Coals**

**BENEFICIATION OF LOW-RANK COALS**

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## BENEFICIATION OF LOW-RANK COALS

### 1.0 INTRODUCTION

Low-rank coals (LRCs) represent nearly half of the estimated coal resources in the world. In many developing nations, LRCs are the only source of low-cost energy. LRCs are typically present in thick seams with less overburden than bituminous coals, making them recoverable by low-cost surface mining. However, even though LRCs burn much more rapidly and completely and usually have much lower sulfur than bituminous coals, they are often regarded as inferior fuels and have not played a significant role in the international steam coal market. LRCs are hindered by the characteristics which differentiate LRCs from bituminous coals, namely, high moisture content, extensive porosity, and high concentration of oxygen functional groups.

In addition, as much as, or more than, 50% of the inorganic material in LRCs occurs as ion-exchangeable cations bound to the organic coal matrix as salts of humic acids or phenolics and cannot be removed by simple physical cleaning methods. Two-thirds of the surface-minable lignite in North Dakota may contain more than 4 wt% Na<sub>2</sub>O in the ash. Because of the limited supply of low-sodium-content lignite and the high cost of conventional means for dealing with the ash-fouling problem, a driving force exists for development and application of a viable method to reduce or eliminate boiler fouling by the reduction of sodium content in the coal.

In addition to ash content, sulfur content is important because of its role in sulfur dioxide emissions. Initially, this program used target sulfur contents of 0.5 wt% sulfur. Another DOE program used a slightly higher sulfur criterion of 1 wt% or less for the design of residential furnaces. Because most sulfur in LRCs occurs as organically bound sulfur and finely disseminated pyritic sulfur, little sulfur removal was expected when cleaning techniques are applied.

During the past six-year period, the EERC demonstrated that low-ash, low-sulfur liquid or dry fuels could be produced from LRCs employing beneficiation techniques such as physical and chemical cleaning, hydrothermal treatment, and agglomeration. The first approach investigated integrating the beneficiation techniques of physical cleaning, chemical cleaning, and hydrothermal treatment to produce a low-ash pumpable coal-water fuel (CWF). The LRC CWFs could compete against bituminous CWFs to replace the more costly fuel oils used in industrial or utility boilers or diesel fuels used in advanced combustion systems. Physical cleaning, to remove discrete minerals, and chemical cleaning, to remove ion-exchangeable elements, were investigated as methods of reducing the ash content to less than 1 wt% on a dry basis. Direct formulation of low-ash LRC CWFs using bituminous CWF preparation techniques was impractical because of the inherent disadvantages of LRCs, namely high moisture content, extensive porosity, and high concentration of oxygen functional groups. Consequently, the EERC development of hot-water drying, a hydrothermal-treatment process, was investigated as a method of mimicking the coalification process to reduce coal hydrophilicity and to improve the water slurryability of LRCs. These processes were developed on a bench scale and, ultimately, the continuous pilot scale to facilitate quantitative production of CWFs for pilot-scale combustion testing. Studies concentrated on the development of methods

and conditions for physical and chemical cleaning and on the relationship of hydrothermal-treatment conditions, particle size, and additives to CWF rheological properties.

The second approach investigated an oil agglomeration process whereby low-ash LRCs could be aggregated into a lump fuel form suitable for transportation by conventional means and utilizable in conventional or advanced combustion systems. Agglomeration was also investigated as a method of producing a low-moisture, high-heating value fuel with resistance to moisture reabsorption similar to that achieved by hydrothermal-drying techniques. A bench-scale process was developed that combined a chemical-cleaning first-stage for ion-exchangeable element removable with a reconstitution second-stage employing a suitable agglomerating oil. Studies concentrated on determining agglomerating oils compatible with the hydrophilic LRC surfaces, developing appropriate agglomerate and process water analytical techniques, quantifying the utilization of agglomerating oil and cleaning chemicals, optimizing agglomerating conditions, and investigating methods of oil recovery from agglomerates.

## **2.0 OBJECTIVES**

The overall objectives of the Low-Rank Coal Beneficiation project were to develop techniques to reduce the moisture and inorganic contents and increase the heating value of LRC to produce high-quality dry products and/or coal-water fuels (CWF). The following areas were investigated during the six-year Low-Rank Coal Beneficiation program:

1. Coal selection for physical, chemical, and hot-water drying beneficiation investigations
2. Physical cleaning for reduction of coal minerals and pyritic sulfur
3. Chemical cleaning for reduction of cationic inorganics, specifically the species associated with boiler deposition
4. Hot-water drying to produce stable, liquid fuel suitable for fuel-oil fired boilers or advanced heat-engines
5. Oil agglomeration to produce a handleable and stable dry fuel from chemically cleaned coal

## **3.0 RESULTS AND DISCUSSION**

### **3.1 Coal Selection for Fuel Production**

Coal selection criteria were based on raw coal analysis; washability data; mine location, with respect to the number of heating degree-days (HDD) greater than 6000; and mine distance from major population centers. A heating degree-day is defined as the unit that represents one degree of decrease from a given point in the mean daily outdoor temperature, in this instance 291 K (18°C).

Seven coals were identified as candidates for study in the LRC beneficiation programs: Beulah and Velva lignites from North Dakota; Jacobs Ranch, Kemmerer, and Skull Point subbituminous coals from Wyoming; Spring Creek subbituminous coal from Montana; and Usibelli subbituminous coal from Alaska. The coals had a sufficient reserve base, met climate requirements, and showed excellent amenability to initial cleaning studies.

Quantitative petrographic analyses were performed to determine the nature and distribution of mineral matter in LRCs. This information was combined with the detailed inorganic analyses for the cleaned LRCs to determine the degree of mineral matter liberation and eventually to predict mineral matter liberation in other LRCs. The three major maceral groups in low-rank coals were found to be 1) huminite, 2) liptinite, and 3) inertinite. Each of these groups had a characteristic range of reflectance values and contained macerals that were in some manner related to one another.

The LRCs tested contained up to 50% of the ash as distinct mineral matter, and the remaining 50% of the ash, which was not detectable by polarizing light microscope, existed as ion-exchangeable cations. This fraction of the inorganics should be relatively easy to remove using ion-exchange methods.

### 3.2 Physical Cleaning

Float-sink washability was the standard method for determining the cleanability of the candidate coals. The various float-sink specific gravity fractions represented theoretical limits attainable by gravity separation. Static separation was most often used for coarse-coal size fractions (9.5 mm to 2.36 mm), whereas a centrifugal separation method was used for fine-coal size fractions (-2.36 mm).

Initial physical cleaning of micronized and combustion-grind LRCs was performed by centrifugal washability testing using Certigrav true specific gravity solutions. Standard ASTM static washability was performed on -6.4-mm x 0.84-mm fractions of select coals to determine the level of cleaning to be expected using pilot-scale, dense-media separation techniques.

Physical cleaning of subbituminous coals using washability techniques removed mostly silicon and iron-bearing minerals and some minerals containing aluminum. Physical cleaning of lignites removed significant portions of all the elements analyzed in the ash, except calcium and magnesium. The results indicate that the inorganic material was found throughout the coal matrix.

Subbituminous coals produced small amounts of 1.3 float, but generally produced significant quantities of product at 1.4 specific gravity. Coal-ash separations at 1.4 specific gravity were variable, with ash reductions ranging from 19 to 66 wt%. North Dakota and Texas lignites were less responsive to washability than higher-rank coals; float yields at 1.3 and 1.4 specific gravity were generally low and ash reductions were much lower than for higher-ranked coals. The possibility exists that a lignite processed in a physical cleaning circuit might behave less predictably than a bituminous coal. This is because of the inherent variability of most lignites and the property changes associated with humidity and temperature. Physical cleaning by washability resulted in ash reductions, yields, and energy recoveries of 25% to 40%, 55% to 72%, and 62% to 74%, respectively.

The candidate subbituminous coals were not evaluated for sulfur reduction by washability physical cleaning because of their low inherent sulfur content. The Beulah lignite with a 1 wt% sulfur content, distributed as 53 wt% pyritic sulfur and 47 wt% organic sulfur, was reduced to 0.44 wt% by physical cleaning. The majority of the sulfur reduction, 95 wt%, was due to removal of pyritic sulfur. The coal yield was 61 wt%, indicating that physical cleaning may be a cost effective method of producing a SO<sub>2</sub> compliant fuel from this lignite.

Froth flotation exhibited little potential for beneficiating low-rank western coals. The frothing agent, methyl isobutyl carbinol (MIBC), which is successfully used in bituminous coal flotation, was generally not effective in producing stable froths with LRCs. The poor performance of MIBC with LRCs was attributed to the hydrophilic LRC surfaces, unlike the more hydrophobic bituminous coals. Other commercial frothing agents designed to stimulate coal floatability by blocking coal surface hydrophilic sites may have potential to improve the floatability of LRCs. Chemical cleaning to remove inorganics associated with the hydrophilic sites was unsuccessfully tested as a method of increasing LRC hydrophobicity and floatability.

### 3.3 Chemical Cleaning

The EERC investigated chemical cleaning to reduce the cation content of LRCs. The method involved mixing pulverized coal with a dilute acid solution for a specified amount of time.

The stability of cations attached to the carboxyl groups in lignite ranges from sodium, as the least stable, to the hydrogen ion, as a nondissociated weak humic acid, as the most stable. Cations, other than the hydrogen ion, form strong electrolytes with the carboxylic group and can be more easily replaced. Sodium removal was a function of particle size and moisture content of the lignite, the ionic strength of the solution, contact time, lignite-to-solution ratio, and the equilibrium between ions in the solid and in solution.

LRC chemical cleaning was performed by leaching with four strong acids (nitric, hydrochloric, sulfuric, and hydrofluoric) and three strong bases (sodium, potassium, and ammonium hydroxide). The acid-leaching process removed mainly sodium, calcium, magnesium, and a small amount of silica. Acid leaching tended to concentrate aluminum and ferric oxide and, to a lesser extent, titanium and potassium oxide. The combination of physical and chemical cleaning concentrated the clean coal ash in silica, aluminum, calcium, and iron. Concentrations of these components indicated that particles such as clays or, in the case of ferric oxide, pyrite were finely disseminated throughout the coals. The overall performance of chemical cleaning were ash reductions of 40 to 60 wt%, yields of 86 to 91 wt%, and energy recoveries of 90% to 93%.

Caustic leaching of LRCs with low-concentration bases, designed to solubilize and separate humic acids from inorganics, proved to be impractical because of extreme difficulty dewatering the product. Also acidification and centrifugation were required to recover the coal from the caustic solution. Due to the extensive amount of processing and difficulty in recovering the coal, caustic leaching was not investigated further.

A preliminary assessment of the colloidal coal-cleaning (CCC) technique for LRCs was evaluated. This process used higher base concentrations and intense shreading using a homogenizer to solubilize the humates. As with caustic leaching, CCC required an acidification step to recover humic acids and repetitive and intense washing to remove residual base cations from the product.

### 3.4 Hot-Water Drying

The EERC pioneered the development of a low-rank coal-water fuel (LRCWF) technology, referred to as hot-water drying (HWD), which can efficiently "dewater" LRCs and enhance the coal surface to allow formulation of an environmentally benign, easily transportable liquid fuel.

HWD is hypothesized to simulate nature's coalification process in a condensed time scale of minutes rather than geological eras. Changes effected by the drying process included irreversible removal of moisture, shrinkage of the pore structure, and enhancement of heating value by removal of oxygen. As a liquid fuel form, HWD LRCs were impervious to dust generation and spontaneous combustion, problems commonplace with raw or conventionally dried LRCs.

HWD enhanced the energy densities of LRCWFs, typically 30% for subbituminous coals, 50% for lignites, and up to 70% for brown coals. Results indicated very slight ash reductions, yields ranging from 80% to 93%, and energy recoveries of 82% to 95%. Ash reductions were primarily by removal of sodium and potassium, which are depositional bad actors during pulverized coal combustion. Depending upon the coal processed, and its associated moisture content, the HWD process was determined to be a potential net water producer, allowing the CWFs to be formulated entirely using the inherent moisture of the raw coal.

Hydrophobic tars, which exude to the surface during the HWD process, were considered to be primary actors in the mechanism of hot-water drying. These tars are hypothesized to cool on the coal surface, sealing micropore entrances and preventing reabsorption of water. In an attempt to identify tar production, solid-state  $^{13}\text{C}$  nuclear magnetic resonance spectrometry (NMR) was used to determine the carbon structure of the raw coals and to detect changes in structure due to hydrothermal treatment. The tars were extracted from raw and HWD coal with methylene chloride and methanol and the residues were characterized using 50-MHz solid-state  $^{13}\text{C}$  NMR spectrometry. The results showed a higher tar yield for the HWD coals relative to the raw coals and a significant decrease in carbonyl/carboxyl and methoxy groups, with little change to the other organic groups, due to HWD. A significant decrease in aliphatic hydrocarbons due to HWD accounted for the increased tar yield.

To further characterize the tar production, a viscosity study was performed using a Haake D100/300 sensor system for the RV100 concentric cylinder viscometer. Viscosity data on raw LRC water slurries were recorded as a function of temperature to 553 K (280°C). In all cases, the viscosity decreased with increased temperature to 483 K (210°C), with the greatest rate of viscosity change occurring between 303 and 363 K (30° and 90°C). The viscosity remained constant or, in some cases, increased as temperature increased from 483 to 553 K (210° to 280°C). In the ranges where the viscosity



increased, tar formation from mild pyrolysis was believed to have contributed to higher viscosities.

#### 3.4.1 Rheological Properties

Knowledge of the sensitivity of CWF flow behavior and viscosity to solids content and temperature is important when designing storage and pumping circuits for slurry-fed combustors and gasifiers. Changes in slurry viscosity and other flow properties, because of variations in solids content and temperature, can drastically alter the energy requirements for pumping and the pressure requirements for atomization. Therefore, the influence of solids content, particle size, and HWD temperature on the CWF flow properties were determined by experiment.

One study identified the effect of solid concentrations on the viscosity of various HWD CWFs over the range of 50 to 1000 Pa·sec. Throughout the entire viscosity regime, the HWD CWFs were characterized as pseudoplastic or shear thinning. Typically viscosity increased at a rate of approximately 75 to 100 Pa·sec in the low-viscosity region (50 to 200 Pa·sec), 100 to 125 Pa·sec in the medium-viscosity region (200 to 500 Pa·sec), and 125 to 175 Pa·sec in the high-viscosity region (500 to 1000 Pa·sec) per 1 wt% increase in solids content. The viscosities were directly affected by coal type and its responsiveness to HWD, HWD temperature, and particle-size distribution.

Viscosity tests were completed on a variety of particle-size distributions (PSD) with a HWD Wyoming subbituminous coal. Depending upon selected PSD, CWF energy densities ranged from 15,100 to 18,800 kJ/kg (6500 to 8100 Btu/lb) on a fuel basis. Optimum particle-size conditions were determined using the Rosin-Rammler equation, with a size-distribution constant of 0.9. An 80/20 mix (80% coarse coal and 20% fine coal) provided a near-optimum particle-size distribution for the bimodal mixture. The average particle size of the coarse coal was 75 microns, while the fine material average particle size was 10 microns. The micronized CWFs had lower solids content and energy densities at equivalent viscosities because of their narrow particle-size distributions. Since reaction time and carbon burnout are critical in advanced combustion systems, micronizing is necessary for bituminous coals and bituminous CWFs. This may not be the case for the highly reactive LRCs and HWD LRCWFs.

Tests on lignite and subbituminous coals also determined the effects of HWD temperature on energy density. Hot-water-dried lignite CWF energy densities increased from 13,000 kJ/kg (5600 Btu/lb) to over 14,200 kJ/kg (6100 Btu/lb), on a fuel basis, when the HWD temperature was increased from 543 to 603 K (270° to 330°C). Subbituminous HWD CWF energy densities improved from 16,300 to 18,600 kJ/kg (7000 to 8000 Btu/lb) at similar test conditions.

#### 3.4.2 Pilot-Scale Continuous Deep Cleaning

Pilot-scale fuel capabilities were developed to prepare sizable quantities of low-ash CWF from LRCs for advanced combustion applications. The preparation scheme included physical and chemical cleaning followed by hot-water drying. Final fuel preparation included size optimization and, in some cases, the use of additives.

Dense-media cone separation was used to physically clean the coal in preparation for clean CWF production. The dense-media cone separator, designed to process coal sized from 6.3 to 0.85 mm, utilized a slurry of magnetite to physically separate the coal from the extraneous mineral matter. The clean coal product was produced at the rate of 150 kg/hr. Prior to any further utilization of the physically cleaned product, the coal was dried to remove surface moisture and pulverized. Pilot-scale chemical cleaning was performed in a downflow column equipped with a mixing shaft and level activated control valve. The pulverized coal, in a dilute slurry, and acid were introduced at the top of the column. Acid cleaning was performed at a rate of 180 kg/hr of coal-water mixture. The sample was centrifuged to recover the acid-cleaned coal for HWD testing. The hot-water-drying system was operated at 270 kg/hr, processing up to 1000 micron coal-water slurry at 513 to 603 K (240° to 330°C) and 2,760 to 15,200 kPa (400 to 2200 psi) for residence times of 1 to 60 minutes.

Good correlation was achieved between bench- and pilot-scale results; CWFs were produced with less than 1.5 wt% ash and energy densities ranging from 13,900 to 18,600 kJ/kg (6000 to 8000 Btu/lb), depending on the particle-size distribution. Coal-water fuel rheological characterization was also performed, with respect to particle-size distribution, additives, and temperature.

#### 3.4.3 Partial Oxidation

Partial oxidation (PO) was investigated as a method of supplying a portion of the required process heat for HWD by in situ combustion of the coal. The process appeared feasible, as combustion was easily initiated using oxygen after first preheating the slurry to 473 K (200°C). However, temperature control was difficult while using a batch system.

The overall economic benefits of PO-HWD over HWD were not determined, although an electrical cost savings would probably be realized by supplying a portion of the thermal requirements by direct (internal) heating. However, additional product gas and PO-HWD coal analysis (proximate, ultimate, and heating value) would have to be performed to determine the cost differential. The results of preliminary calculations indicated an approximate process heat cost savings of 35%.

The PO-HWD coals, to a limited extent, also had enhanced float-sink washability, relative to conventional HWD coal. Presumably, the surface tars normally present after conventional HWD were consumed during PO. Consequently, any previous inhibition of mineral liberation because of the tar coating was somewhat alleviated by PO. Product yields and heating values were much lower with PO products than with HWD products due to the consumption of coal by combustion.

#### 3.4.4 Chemical Additives

Additive packages were identified that would allow the LRCWFs to meet DOE energy density, flow behavior, and storage life specifications. A screening study was performed to determine the effectiveness of chemical additives for increasing the solids loadings for the clean CWFs. Generally, the nonionic surfactants were more effective than anionic dispersants. Anionic dispersants were ineffective, as no increase in solids content was realized for the two

types tested. The anionic additives disperse and stabilize solids by the principles of electrostatic dispersion or positive-negative charge. This phenomenon was adversely affected by the ionic strength of the CWF aqueous medium. The ionic strength was possibly caused by residual acid from the chemical cleaning and other water-soluble ions in the aqueous medium of the CWF. The pH of the CWF from the clean products ranged from 4 to 5, rendering the anionic additives ineffective. The nonionic surfactants behave on the principles of steric dispersion and stabilization, which are physical phenomena. Therefore, the nonionic additives were generally insensitive to pH changes or ionic strength in aqueous medium. The high molecular weight BASF F series additives—copolymers of ethylene oxide and propylene oxide—were effective on a clean lignite in the screening tests.

Long-term stability was a concern with CWFs, especially when considering the fuel for residential, commercial, or industrial combustion applications. Depending on the percentages of soluble, multivalent cations in the coal, HWD promoted stability in CWFs prepared from LRCs by leaching available cations out of the coal. Studies indicated that a 0.2 wt% xanthan gum loading was sufficient for 6-month storage stability of the cleaned lignite CWF. In addition to stabilization compounds, formaldehyde added at 0.1 wt% was necessary to prevent mold growth.

Testing also investigated CWF's resistance to rheological and stability variations during freeze-thaw cycling. Shear stress versus shear rate relationships identified the before-and-after flow behavior characteristics of the fuel. Freeze-thaw testing indicated slight increases in solids content and viscosity ranging from 5% to 20% above those of the original sample. These increases were attributed mainly to evaporation during the testing process. The low solids and viscosity increases indicated that the CWFs were relatively unaffected by freeze-thaw. The CWFs were also stable after freezing, although rheologies of the HWD sample exhibited a slight difference in flow behavior. The sample, pseudoplastic before freezing, exhibited yield-pseudoplastic characteristics after freezing. Therefore, coal-water mixtures containing additives and stabilizers can be frozen, thawed, and remixed without any major stability or viscosity changes occurring to the fuel.

#### 3.4.5 Coal-Water Fuel Process Water Treatment

The production of CWF by the hot-water, coal-drying process resulted in the generation of process effluent water. Due to the hydrothermal coal dewatering process, a portion of the sodium and other water-soluble inorganic constituents are transferred from the coal particles to the aqueous medium. Additionally, water-soluble organic compounds are extracted from the coal particles by the process water. Mechanical concentration of the processed coal produces a damp HWD coal and a contaminated effluent water by-product (centrate), which contains coal fines, dissolved inorganics, and water-soluble organics.

The centrate from mechanical concentration (continuous centrifugation), collected after hydrothermal processing of a subbituminous coal, was used for treatability studies. The treatment process addressed the reduction of suspended solids prior to subsequent secondary and tertiary treatment processes. Two methods of suspended solids removal were investigated for

CWF product recovery and centrate pretreatment: chemical coagulation/precipitation, and ultrafiltration.

Initial jar tests with acidification of the raw CWF centrate resulted in solids separation of 200-mL solids/L wastewater at a dosage of 1-mL/L concentrated sulfuric acid. Due to the encouraging initial jar-testing results on fresh centrate samples, additional efforts should be directed at coagulation/precipitation for the separation of colloidal suspended solids from fresh CWF centrate.

Ultrafiltration used a membrane process to separate solids and high molecular weight dissolved materials from the centrate. Results indicated that the flux (filtration rate) remained relatively stable for the 4 hours of testing. A computer model, based on several effects, was formulated to predict the flux through the membranes. Preliminary results indicated ultrafiltration is a technically viable means for removal and recovery of solids from CWF centrates; however, more testing should be completed because a major concern with membrane-based filtration systems is the length of time that the unit can run between cleanings without significant loss in filtration rates.

An activated sludge system was selected to evaluate aerobic biological system secondary treatment of HWD process water. The activated sludge process utilized a suspended, mixed growth of aerobic microorganisms that used the organic materials in wastewater as substrates. Testing was conducted to determine removal rates of biochemical oxygen demand ( $BOD_5$ ), chemical oxygen demand (COD), and total organic carbon (TOC). At steady-state operating conditions, average  $BOD_5$  removal was 95.7% and COD and TOC removal varied from 20% to 38% and 40% to 60%, respectively, depending upon cell residence times.

### 3.5 Acid Cleaning/Oil Agglomeration

#### 3.5.1 Development of Experimental Procedure

The EERC agglomeration process, in its present stage of development, incorporates a chemical-cleaning first-stage with a fine, clean coal reconstitution second-stage. During chemical cleaning, 1-part pulverized coal and 2-parts dilute acid are intensely mixed using a high-shear homogenizer to liberate the organically associated alkali and alkaline earth metals plus other acid-soluble minerals. The fine, acid-cleaned coal is recovered by adding a specified quantity of agglomerating oil. Agitation by stirring causes wetting of the coal particles by the oil; formation of agglomerates occurs due to repeated collisions of the oiled coal particles. The 2- to 4-mm agglomerates are separated from the chemically liberated inorganics, which remain solubilized in the process water by a simple screening technique.

Preliminary development work on the EERC agglomeration process was performed by Knudson and Mack to obtain rudimentary information on the effect of particle size, oil-to-coal ratios, and agglomeration mixing speeds and times. Initially, chemical cleaning was facilitated by sonication, which was presumed to aid separation of discrete mineral matter. However, after limited testing, sonication was considered impractical and unscalable to pilot, development, or production size. Furthermore, the benefits of sonication for enhanced mineral separation were not definitively proven. Sonication was first replaced by low-speed T-bar mixing, then ultimately replaced with high-shear

homogenizer mixing. This latter method was presumed to be superior to sonication or low-speed mixing for ensuring penetration of the acid into the pores of the coal. A second major process modification was the elimination of surfactant as an agglomeration pretreatment. The surfactant, typically Triton X-100, was presumed to lower the solution surface tension and aid wetting of the coal surface by the agglomerating oil. However, the water solubility and LRC compatibility of the preferred agglomerating oils facilitated successful agglomeration without the surfactant. Elimination of the surfactant, used in concentrations up to 60 kg/metric ton (120-lb/ton) coal, was also considered to benefit process economics.

Statistical matrix testing was used as a method to optimize the agglomeration of Beulah lignite with crude phenol (a coal-derived oil). The parameters were particle-size, acid contact time, chemical-cleaning mixing speed, oil mixing time, agglomeration mixing speed, acid strength, and oil concentration. The statistical matrix tests established levels for chemical-cleaning and agglomeration parameters, some of which are still used. Preferred coal sizes were  $-0.59 \text{ mm} \times 0.075 \text{ mm}$ , as particles below  $0.075 \text{ mm}$  resulted in low agglomerate yields. An oil mix time of 2 minutes was optimum for maximizing ash reduction, although, typically, an agglomeration time of 5 minutes maximized recovery of coal solids. Optimum agglomerating oil mix speeds were 400 to 800 rpm, with the latter value more commonly used, and the optimum oil-to-coal ratio was 1 mL/g. Depending on the measured response during matrix testing, the optimum acid-cleaning mixing speed and time gave significantly varying results. The optimum levels for high-shear mixing speed and acid-cleaning time to maximize ash reduction, as determined by one-at-a-time experiments, were 5000 rpm and 1 to 2 minutes, respectively.

The parametric values obtained with the Beulah lignite, i.e., acid concentrations between 0.75 and 6.0 wt% and oil-to-coal ratios of 1 mL/g, were used as initial parametric levels when evaluating new coals. The optimum oil level for maximizing coal recovery and the optimum acid concentration for maximizing ash reduction were typically obtained by one-at-a-time experiments.

Strong acids—nitric, hydrochloric, and sulfuric—were equally effective at reducing the inorganic contents of LRCs over the range of 0.75 to 6.0 wt% acid. Unrinsed samples of LRCs cleaned with these acids had higher concentrations of nitrogen (probably as  $\text{NO}_3^-$ ), chlorine (as  $\text{Cl}^-$ ), or sulfur (as  $\text{CaSO}_4$ ) compared to the raw coals. The  $\text{NO}_3^-$  and  $\text{Cl}^-$  were easily removed by water rinsing; the removal of  $\text{CaSO}_4$  required secondary washing with a dilute solution of formic or nitric acid. Because of the negatives associated with high chlorine and sulfur levels, nitric acid became the preferred acid for chemical cleaning.

The capacity of the batch, bench-scale agglomeration process, initially developed using 50 grams of coal per test, was successively increased by factors of 2, 4, and 30 times. Typically, agglomeration tests to assess new coals or oils were performed with 50 grams of coal per test. Sufficient quantities of agglomerates were produced using 200 grams of coal per test to facilitate all analyses required for subsequent oil, water, and solids balances. Sufficient quantities of agglomerates were produced at 1500 grams of coal per test to allow parametric thermal deoiling tests and stability tests.

### 3.5.2 Development of Agglomerate and Process Water Analytical Techniques

Concurrent with the development of the chemical-cleaning/oil agglomeration process, several analytical techniques were evaluated for determining the oil content of agglomerates (raw, air-dried, deoiled) and process water and for determining the residual acid content of process water. These analyses were presumed critical for determining the consumption of the more costly raw materials—oil and acid.

Thermogravimetric analysis (TGA) was the first method evaluated for determining oil content of the agglomerates. TGA directly determined the fractions of the light oil, oil, volatile matter, fixed carbon, and ash. The sum of the light oil plus oil fractions was presumed to represent the agglomerate oil content. However, fixed-carbon recoveries calculated with the TGA results were generally well in excess of 100 wt% indicating 1) the agglomerating oil contained a fraction in the fixed-carbon distillation range, and 2) agglomerating oil polymerization may have occurred during the rapid TGA, resulting in further production of fixed carbon. Agglomerate oil contents were also calculated by difference from the sum of the mass of light oil, oil, volatile matter, fixed carbon, and ash in the agglomerates and raw coal. The calculation methods resulted in oil contents at least 8 to 11 wt% higher than oil contents directly obtained from TGA. Consequently, pending appropriate modifications, TGA was considered unsatisfactory for directly or indirectly determining agglomerate oil content. Nonaqueous titration to measure cresol content and tetrahydrofuran (THF) solubility, also tested as agglomerate oil content measurement methods, proved to be inadequate. The most recently evaluated technique, Soxhlet extraction, appeared suitable for analyzing raw and air-dried agglomerates. Thermally treated agglomerates could not be analyzed for oil content by Soxhlet extraction because heat treatment is hypothesized to polymerize some of the agglomerating oil, inhibiting complete elution by the extraction solvent.

Initially, ASTM method D271 and TGA analysis were evaluated for determining the moisture content of air-dried agglomerates. These weight-loss measurement techniques proved unreliable because of the concurrent loss of agglomerating oil. The Karl Fischer titrimetric analysis technique was ideal for moisture analysis because it could be performed in the presence of volatile organics. Azeotropic distillation, used in conjunction with the Soxhlet extraction method, also proved suitable for determining agglomerate moisture content. Presently, direct comparisons have not been made among the latter two methods; however, advantages of Karl Fischer analysis include less waste and faster analysis time compared to azeotropic distillation. One drawback to the former method was the small sample size, which can produce results unrepresentative of the bulk agglomeration test sample.

Two methods were investigated for measuring the residual agglomerating oil content in the process water: total carbon (TC) analysis and solvent extraction. Total carbon was a fast, very reproducible combustion/infrared method for determining the carbon content of water. The total oil content of the water was calculated from TC analysis presuming that the oil composition (i.e., wt% carbon) in the process water was equivalent to the initial agglomerating oil. Based on preliminary oil balances with mono- and multicomponent agglomerating oils, TC analysis appeared satisfactory for

indirectly determining the agglomerating oil content of process water. Solvent extraction, a common technique for process water oil recovery, was investigated in a single test as an analytical technique. The calculated oil content, as determined from solvent extractions, was approximately 2.5 times higher than that achieved by TC analysis.

Acid consumption during the chemical-cleaning stage was determined by comparing the molar strengths of the initial and final acid-cleaning solutions. Titration of the acid solution with a dilute base was performed after chemical cleaning, but prior to agglomeration to eliminate the interference of the agglomerating oils. The method of titration was a highly repeatable technique for determining acid consumption.

### 3.5.3 Agglomerating Oils Tested and Oil Characterization

A number of agglomerating oils were evaluated as primary bridging liquids during the development of the chemical-cleaning/oil agglomeration process. These oils included the coal gasification-derived crude phenol and tar oil streams, liquefaction-derived V161 and V178 naphthas, several mild gasification-derived tars, a used petroleum-based crankcase oil, a reagent grade *m*-cresol oil, and a commercial cresylic acid. Crude phenol or a crude phenol/tar oil blend were primarily used during development of the agglomeration process and the associated analytical techniques. The other agglomerating oils were tested to assess the versatility of the process.

Several agglomerating oils were evaluated as binding oils to be used in conjunction with the primary agglomerating oil or bridging liquid. These oils included tar oil, creosote oil (coal-derived), asphalt, and red crude and decant oil (both petroleum-based).

Crude phenol or crude phenol/tar oil were the agglomerating oils against which the other oils were compared. The crude phenol, tar oil, crude phenol/tar oil, *m*-cresol, and cresylic acid were determined to be very effective for agglomerating chemically cleaned LRCs using low-shear mixing (400 to 800 rpm). The time required to achieve agglomeration varied between oils and ranged from 2 to 5 minutes for crude phenol, tar oil, crude phenol/tar oil, and *m*-cresol to as high as 7 to 15 minutes for cresylic acid. The agglomerating oil/coal ratio also varied, ranging from 0.6 to 0.7 mL/g for cresylic acid to 0.9 to 1.0 mL/g for the other low-shear compatible oils.

Agglomeration was not possible at low-shear mixing conditions using the liquefaction-derived oils, mild gasification-derived tars, or used crankcase oil. Surfactants or high-shear mixing were required to effect agglomeration with these tars/oils. Surfactant concentrations up to 40 kg/metric ton (80 lb/ton) of coal aided agglomeration using the liquefaction naphthas at oil-to-coal ratios of 0.5 to 0.6 mL/g. Mild gasification tars, thinned in a solvent (butanol or pentane), successfully agglomerated LRCs at concentrations of 0.6 g-tar/g coal when using high-shear mixing. The used crankcase oil, at oil-to-coal ratios of only 0.3 mL/g, agglomerated LRCs only after high-shear mixing.

Attempts were made to correlate the agglomeration conditions, i.e., low-shear mixing versus high-shear mixing or surfactant addition, against the composition of the agglomerating oils; i.e. the polar content and oxygen

polar functionalities, such as the hydroxyl group (OH). Agglomerating oil aliphatics, branched aliphatics, aromatics, and polar contents were determined by open-column chromatography, and oxygen contents were determined by difference using ASTM method D3176 ultimate analysis.

The agglomerating oils, which required only low-shear mixing to effect agglomeration, had the highest polar and oxygen contents; the converse was true for the tars/oils requiring surfactants or high-shear mixing. The relationship between agglomeration conditions and oil composition appeared to be more dependent upon oxygen content and less dependent upon polar content. The polar contents of the most effective oils ranged from 80 wt% for the crude phenol/tar oil mixture to 100 wt% for the "pure" oil, *m*-cresol. The polar contents of the less effective oils ranged from 13 wt% for used crankcase oil to 54 wt% for the mild gasification tars. The oxygen contents of the more effective oils did not vary significantly and ranged from 12 to 15 wt%. The oxygen contents of the less effective oils were considerably lower and ranged from only 0.7 to 3.1 wt%. Based on preliminary testing, determination of polar and oxygen contents may be a useful method for screening oils for use in agglomeration processes employing low-shear mixing.

#### 3.5.4 Characteristics of Chemically Cleaned and Agglomerated LRCs

Agglomeration was successfully accomplished with a number of LRCs, including Morwell and Yallourn brown coals from Australia; Indian Head, Beulah, and Center lignites from North Dakota; Calvert lignite from Texas; Wyodak, Fort Union, Eagle Butte, and Kemmerer subbituminous from Wyoming; Spring Creek subbituminous from Montana; Beluga subbituminous from Alaska; and a lignite from Czechoslovakia.

The majority of agglomeration tests were performed with the baseline Beulah lignite using crude phenol or blends of crude phenol as a bridging liquid and low concentrations of other coal- or petroleum-derived oils as binding oils. The tests with the other LRCs used crude phenol or crude phenol/tar oil as the agglomerating oil. Typically, the binding oils were mixed with the bridging liquids in concentrations of 3 to 9 wt%. The concept of blending a bridging and binding oil was developed presuming that thermal deoiling would be required to recover the bridging liquid. The binding oil would add strength to the agglomerates following thermal deoiling; however, the validity of this concept was not ascertained pending the development of an adequate thermal deoiling system and accurate, repeatable agglomerate analysis and strength determination techniques.

Chemical cleaning of the LRCs prior to agglomeration resulted in significant reduction of ion-exchangeable inorganics, principally sodium, magnesium, potassium, and calcium; the discrete mineral content was increased as a result. Maximum LRC inorganic reduction was typically achieved at acid concentrations between 3.0 and 6.0 wt%. The maximum reduction in ASTM ash content typically ranged from 65 to 80 wt% for North Dakota lignites; the ash reductions were only 30 to 40 wt% with the Texas lignite because the ash in this coal has a lower ion-exchangeable inorganic content. Similarly, because the ASTM ashes of the subbituminous coal studied had a lower proportion of ion-exchangeable inorganics compared to the lignite coal ashes, the maximum ash reductions for the subbituminous coals typically ranged from 35 to 50 wt%. The ASTM ash contents of air-dried North Dakota lignite agglomerates were as low as



1.0 to 1.5 wt%, and air-dried agglomerates made with Wyoming and Montana subbituminous coals were as low as 1.5 to 2.0 wt%. At the acid concentrations required for maximum inorganic reduction, the removal of sodium approached 100 wt%, and the removal of magnesium and calcium approached 70 to 80 wt%.

The air-dried agglomerates produced from all LRCs, even brown coals, were characterized by low moisture contents, 2 to 5 wt%. The moisture contents of the raw coals, in comparison, ranged from 20 to 25 wt% for the subbituminous coals, 30 to 35 wt% for the lignites, and between 50 and 65 wt% for the brown coals.

The dewatering during agglomeration and subsequent air-drying significantly increased the fuel heating value relative to the raw coals. The heating values of the air-dried agglomerates ranged from approximately 27,900 to 30,200 kJ/kg (12,000 to 13,000 Btu/lb). The raw coal heating values, in comparison, ranged from 14,900 to 17,200 kJ/kg (6400 to 7400 Btu/lb) for the lignites and 18,600 to 20,900 kJ/kg (8000 to 9000 Btu/lb) for the subbituminous coals.

### 3.5.5 Material Balances, Consumption of Agglomerating Oil and Acid

The most reasonable oil, water, and solids balances were attained using azeotropic distillation and Soxhlet extraction to determine agglomerate moisture and oil content. The oil content of the process water was determined using total carbon analysis. The raw agglomerate moisture content ranged from 28 to 32 wt%, and the raw agglomerate oil content was approximately 37 wt%. This concentration of oil represented about 83 to 87 wt% of the oil added during the agglomeration process. The balance of the oil, 13 to 17 wt%, remained solubilized in the process water. Depending upon the volume of water added during rinsing and washing, the concentration of oil in the process water ranged from ~11,500 to 16,500 mg/L.

Air-drying the raw agglomerates resulted in significant evaporation of surface moisture and agglomerating oil. Approximately 27 to 32 wt% of the agglomerating oil evaporated, and between 85 to 95 wt% of the moisture evaporated. The significant evaporation of moisture during air-drying, relative to the evaporation of oil, resulted in a concentration of oil with the oil content typically reaching 41 to 43 wt%.

Acid consumptions and acid costs were determined for cleaning Beulah lignite (7.4 wt% ash, moisture-free [mf]) and Spring Creek subbituminous (5.1 wt% ash, mf) using nitric acid with concentrations of 0.75 to 6.0 wt%. Ash contents of acid-cleaned Beulah ranged from 6.3 to 3.1 wt% (mf), and the acid consumption associated with these ash contents ranged from 2.1 to 8.5 lb of concentrated acid per 100 lb of coal. Similarly, ash contents of acid-cleaned Spring Creek ranged from 4.2 to 2.9 wt% (mf), and the acid consumption ranged from 2.3 to 7.9 lb of concentrated acid per 100 lb of coal.

The nitric acid costs for cleaning Beulah lignite and Spring Creek subbituminous coal, over the range of acid concentrations studied, were \$4 to \$17/ton coal and \$5 to \$14/ton coal, respectively.

## 4.0 CONCLUSIONS

Initial petrographic analyses were investigated to determine the distribution and size of mineral matter in several LRCs. These analyses were used as a guide for the degree of grinding necessary to achieve mineral liberation. Clean coals with less than 2 wt% ash on a dry basis were produced on the bench scale and continuous pilot scale using physical- and chemical-cleaning techniques. Selectivity of the cleaning processes were quite different for the various LRCs. CWFs—with less than 1 wt% ash, energy densities over 17,400 kJ/kg (7500 Btu/lb), and a solids loading over 60 wt%—were prepared after optimizing particle-packing efficiency and using additives. The flow behavior of the CWFs with the complete additive package presented no serious handling problems, as the fuels exhibited near Newtonian flow behavior over the shear-rate range tested. Dilatant flow behavior resulted if the particle size was too small.

Ultrafiltration was a technically viable means for removal and recovery of suspended solids from centrifuge concentrates. Activated sludge treatment of the ultrafilter permeate was effective at removing BOD<sub>5</sub>.

The low initial cost of the raw LRCs improved the economic feasibility of producing low-ash CWF by offsetting the relative expense of chemical cleaning and reagents in the processing scenario. The additional cost of micronizing was not onerously significant. However, micronizing adversely affected product solids concentration and flow behavior. Until process and product refinements are made in the micronizing area, it is recommended that this process addition be avoided.

The EERC chemical-cleaning/oil agglomeration process was successfully used on brown, lignitic, and subbituminous coals. Nitric, hydrochloric, and sulfuric acids were equally effective in reducing the inorganic content of LRCs. Water washing removed nitrate and chloride ions, which adhered to the nitric and hydrochloric acid-cleaned coals. Secondary acid washing removed calcium sulfate that precipitated as a result of using sulfuric acid for chemical cleaning. Removal of coal inorganics was maximized within the range of 0.75 to 6.0 wt% acid. The preferred oils for agglomerating LRCs were characterized by high polar and oxygen contents and were typically coal-derived oils. The preferred oils required only low-shear mixing to cause LRC agglomeration.

ASTM and TGA proximate analysis techniques were inappropriate for determining the moisture and oil contents of agglomerates. Karl Fischer titration and azeotropic distillation were suitable for determining agglomerate moisture content, and Soxhlet extraction was suitable for determining agglomerate oil content. Total carbon analysis was suitable for determining the residual oil content of the process water.

The chemical-cleaning/oil agglomeration process resulted in significant dewatering (moisture reduction) of LRCs. Inorganic reduction was typically higher for lignites compared to subbituminous coals because of the higher concentration of ion-exchangeable inorganics in the lignites.

## 5.0 RECOMMENDATIONS

Qualitative and quantitative analysis of the hot-water-dried products should be performed in order to understand mechanisms such as tar evolution. Froth flotation testing should be conducted on the dilute HWD product slurry. It has been stated that the HWD coal becomes hydrophobic in nature following hot-water drying. Therefore, froth flotation should be more effective on this product rather than the hydrophilic raw LRC. The only concern is that the tar evolved during the HWD may trap minerals in the coal particles, reducing the separation of coal and minerals.

Pilot-scale HWD testing should be used to address heat-transfer issues in order to integrate a process effluent heat exchange system and improve process efficiencies. An extended run on the pilot-scale unit should be performed to address issues of heat capacity, thermoconductivity, and any potential scaling problems during heating.

Thermal deoiling for agglomerating oil recovery needs to be more thoroughly investigated. The recovered oils should be characterized to determine suitability for recycle or sale as an upgraded product. Thermally deoiled agglomerates should be evaluated for strength and stability toward dust generation, spontaneous combustion, and moisture reabsorption. An appropriate bridging/binding oil combination should be selected based on strength and stability of the agglomerates. Combustion testing should be performed on thermally deoiled agglomerates to determine the reduction in depositional tendencies due to reduction of the ion-exchangeable inorganic content. A preliminary plant design and associated economics should be made on a nominally sized continuous agglomeration plant with and without chemical cleaning.

In order to characterize the behavior of the various ash components in selected coals and their beneficiated products, a detailed characterization of the coals should be performed before and after beneficiation. The methods of characterization should include computer-controlled scanning electron microscopy, chemical fractionation, and standard ASTM techniques. An additional objective would be to establish predictive methods to evaluate ash behavior from cleaned and beneficiated LRCs and to design new beneficiation processes and/or optimize current procedures. Detailed characterization techniques will provide insight into the effects of various beneficiation processes and help develop new methods.

These and other process developments are viewed as critical to further establish the usage of LRC and create new domestic and international markets.

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**4.3 Combustion Characterization of Low-Rank Fuels  
(COMPLETED 10-31-90)**

**4.4 Diesel Utilization of Low-Rank Coals  
(COMPLETED 12-31-90)**

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**4.5 Produce and Characterize HWD Fuels for Heat Engine Applications  
(COMPLETED 10-31-90)**



#### **4.6 Nitrous Oxide Emissions**

**Final Report IS NOT Included  
(Project was extended to September 30, 1993)**

## **4.7 Pressurized Fluidized-Bed Combustion**

**PRESSURIZED FLUIDIZED-BED COMBUSTION**

Final Technical Progress Report  
for the Period July 1, 1990, through September 30, 1992

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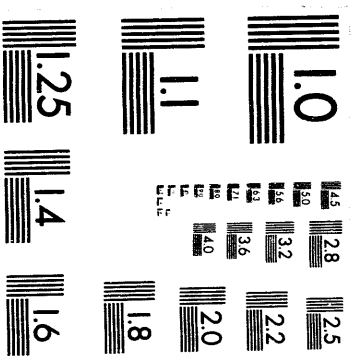
Work Performed under Cooperative Agreement No. DE-FC21-86MC10637

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## PRESSURIZED FLUIDIZED-BED COMBUSTION

### 1.0 BACKGROUND

Pressurized fluidized-bed combustion (PFBC) has several advantages that make it attractive as a technology of the future. Some of these advantages are:

- Increased efficiency and reduced capital and generating costs compared to pc-fired boilers equipped with flue gas desulfurization (FGD).
- Modular units without the usual economy-of-scale penalty.
- Reduced combustor size permitting shop fabrication and field erection, thereby greatly shortening construction lead time.
- High-sulfur fuels burned in the presence of sorbent in the FBC eliminate the need for FGD.
- Reduced combustion temperature (1400°-1700°F versus 3000°F for a pulverized coal-fired boiler) which results in significant reduction of NO<sub>x</sub> emissions.
- Increased heat-transfer rate to the working fluid.
- Increased fuel versatility.
- Easily handled by-product material consisting of clinker-free, granular, smooth-flowing ash which may be easily disposed of in a landfill or potentially sold for industrial or agricultural applications.

Major technical uncertainties identified by industry as critical areas for PFBC commercialization are:

- Hot-gas cleanup for gas turbine protection, with particular reference to coal alkalies.
- Materials survivability for heat exchanger, gas turbine, and solids handling equipment.
- Solids handling improvement in feeding, distribution, and bed removal.
- Combustor configuration, including the heat-transfer bundles, distributor plate, fuels utilization, and operational parameters.

Some of these problems are being addressed by programs such as those at Grimethorpe and New York University. Others will hopefully be resolved during operation of the three demonstration plants using first-generation technology. These plants are the AEP 70-MW<sub>e</sub> Tidd Station at Brilliant, Ohio; the 79-MW<sub>e</sub> Escatron Power Plant in Spain; and the 135-MW<sub>e</sub> Energi Vartan plant in Stockholm, Sweden. Although these plants show improved efficiency over atmospheric systems, they are still significantly below gas-turbine



efficiency. In an attempt to increase these efficiencies, several companies are actively involved in the development of second-generation PFBC systems. The goals of the second-generation system are a 45% coal-to-electricity efficiency, 20% cost-of-electricity advantage over pc-fired systems, modular design for shop fabrication, to meet or exceed new source performance standards (NSPS), and the ability to operate on a wide range of coals.

## **2.0 GOALS AND OBJECTIVES**

The overall goal of the PFBC program at the Energy and Environmental Research Center (EERC) is to generate both fundamental and process information that will foster the development of an economical and environmentally acceptable second-generation PFBC concept. The goal is to focus on generic issues, such as the fate of alkali in PFBC systems, sorbent utilization, and carbonizer performance, while providing input to assist in the development of second-generation systems.

During the last two years of this Cooperative Agreement (7/90-6/92), work focused on three main areas: carbonizer performance, fate of alkali, and increased sorbent utilization. Objectives are discussed below.

### **2.1 Carbonizer Performance Evaluation**

In order for a second-generation PFBC to achieve 45% efficiency, it is likely that the coal must be partially gasified in a carbonizer or a partial gasifier and the char residue burned in the PFBC. This will produce gas streams that can be cleaned at an intermediate temperature (e.g., 1600°F) and then afterburned to obtain temperatures higher than those obtainable directly from the PFBC, thereby increasing the efficiency of the gas turbine. Information needs to be generated to determine the extent of gasification desired to obtain the highest efficiency while maintaining the benefits of the PFBC in terms of meeting environmental standards. The partial gasification step is referred to here as carbonization.

The goal of this task is to use the existing EERC mild gasification reactor, with some modification, to develop a database at temperatures and pressures representative of those for a second-generation system. Gas, tar, and liquid yields for selected coals will be determined. The fate of sulfur and alkali will be investigated. The amount of tar generated, its properties, and the elimination of tar will be studied to determine whether or not it will pose problems in the hot-gas cleanup device.

### **2.2 Fate of Alkali in PFBC Systems**

Alkali in the coal, especially that organically bound, will volatilize even at the low temperatures typical of a fluid-bed gasifier or combustor. This alkali can cause problems in both the filter media and the turbine. The EERC will focus on developing an understanding of how the alkalies are released so that methods of rendering them harmless can be found. Alkali gettering to keep the alkali in the bed is one potential method of protecting the filter and turbine. Some work will be done on the pilot-scale bubbling and circulating atmospheric fluid beds. Because the vapor pressures of the alkali species are low and not greatly influenced by pressure, it is felt that

data from the atmospheric units will be applicable to pressurized systems. Work will also be done on the bench-scale pressurized reactor. PHOEBE, a thermodynamic code for predicting gas-solid-liquid-equilibrium stages, will be used as a tool to help predict trends with changing operating conditions and coal types.

### 2.3 Bench-Scale Reactor Testing

A bench-scale reactor will be built to study PFBC reaction kinetics and conversions. The reactor will be designed around an already existing piece of equipment to minimize costs. Design efforts will attempt to minimize the impacts of the small size on the usefulness of the data, while providing for a wide range of conditions applicable to combustion and gasification in bubbling and entrained/circulating fluidized beds. A 3-inch-ID reactor is envisioned. This reactor will be used to study sorbent utilization and alkali gettering. It is important to improve sorbent utilization and minimize the amount of sorbent feed and waste disposal. Extending the operating conditions where conventional sorbents are effective may help improve the overall efficiency of the PFBC. If properly designed, it is envisioned that this reactor could also be used for studying  $N_2O$  emissions, if time and budget allow.

## 3.0 RESULTS AND DISCUSSION

### 3.1 Carbonizer Performance Evaluation

#### 3.1.1 Addition of the 4-lb/hr Continuous Fluidized-Bed Reactor (CFBR) to the Test Matrix

Limited operation of the EERC 4-lb/hr continuous gasifier was added to the experimental matrix due to delays encountered with the certification process for the primary gasification vessel and with delivery of equipment needed for system modifications. A description of this unit is provided in Appendix B. The rationale was that use of the smaller unit would enable the effects of various operating conditions to be investigated more easily, resulting in more efficient testing on the 100-lb/hr unit. The information gathered during the 4-lb/hr tests was to be used to determine the conditions at which the 100-lb/hr unit would yield the most useful data. Because it is possible to obtain only three data points each week with the 100-lb/hr unit, it was critical that the most meaningful test points be run on this unit.

#### 3.1.2 Results of Testing Performed on the 4-lb/hr CFBR

Five tests were performed on the 4-lb/hr unit. The conditions of these tests are given in Table 1. The first and second tests (using Wyodak subbituminous coal) were successfully completed. During the third test, the Pittsburgh No. 8 coal agglomerated approximately 15 minutes into the run. An error in prerun calculations had set the actual Ca/S ratio at 0.45 rather than the planned 1.75. The low dolomite add rate may have increased the tendency for the high-swelling Pittsburgh No. 8 coal to form agglomerates during carbonization.

TABLE 1

Tests Run in the 4-lb/hr CFBR

Run	M169	M170	M171	M172	M173
Coal	Wyo <sup>a</sup>	Wyo	Pitts 8 <sup>b</sup>	Wyo	Pitts 8
Avg. Bed Temp., °F	1562	1562	1562	1562	1562
Pressure, psig	25	55	55	165	150
Coal Size, inch	-¼	-¼	-¼	-¼	-¼
Dolomite size, mesh	-30	-30	-30	-30	-30
Dolomite/Coal, wt. ratio		1.00	4.40		

<sup>a</sup> Wyodak subbituminous coal.

<sup>b</sup> Pittsburgh No. 8 bituminous coal.

Run M172 was initiated using Wyodak subbituminous coal. Steady-state conditions were reached at 1562°F and 150 psig. Run M173 began when the coal hopper was switched and Pittsburgh No. 8 coal was fed. Bed agglomeration occurred after approximately 30 minutes, forcing shutdown of the run.

Data which could be reduced indicated that the results of the carbonizer testing agreed reasonably well with the results seen during mild gasification testing. Tar yields in the carbonizer operational mode were low to nonexistent. Partial-gasification-produced char yields were similar to those produced during mild gasification, with the exception that the pressurized carbonizer char contained less volatiles.

### 3.1.3 Description of the 100-lb/hr Mild Gasification Process Development Unit (MGPDU)

The MGPDU was designed to process 100 lb/hr of feed coal on a dry basis and is capable of drying, carbonizing, and calcining both caking and non-caking coals in pressurized fluid-bed reactors as well as separating char, liquid, and gaseous products. The system was designed for integrated operation, and because provisions were made so that carbonization could take place without the use of the calciner, the unit works well within the second-generation PFBC program. A description of the MGPDU is presented in Appendix A.

#### 3.1.3.1 Modifications Required to Integrate the 100-lb/hr MGPDU into the Second-Generation PFBC Carbonizer Program

Several minor modifications to the MGPDU were required to ensure that the unit could be operated at the carbonizer test conditions of 150 psi and 1600°F. The modifications included the replacement of all slide valves on the primary cyclone, secondary cyclone, coal feed system, and char product receiver with ball valves. Pressurized site ports were added to the coal feed system and the natural gas burner flame detection sensor. A pressurized burner was constructed and used to replace the existing system. The conical section of the pressurized coal hopper, the bottom of the char receiver, and the primary cyclone inlet wall were reinforced. The first water scrubber gas/liquid separation cyclone was modified to prevent the water entrainment

observed during cold-flow model testing. A small gas slipstream condensation train was added to assist in the accurate determination of tar yields. Minor process control reprogramming was performed so that the carbonizer could operate with heat generation from either a natural gas burner or by internal oxidation using oxygen or air. A natural gas compressor was refurbished and piped in for this purpose. All flanges and closures were reevaluated and retorqued.

### 3.1.3.2 ASME Boiler Code Certification

The mild gasifier system (carbonizer, calciner, and support systems) was originally designed for service at atmospheric pressure. In order to determine that the system was safe for operation at pressures up to 150 psig and to comply with the North Dakota State Boiler laws, it was necessary to perform a thorough analysis of the vessels and associated piping systems. Components of the system that met the legal definition of an unfired pressure vessel according to North Dakota State Boiler laws were analyzed in accordance with the ASME Boiler Pressure Vessel Code Section VIII, Divisions 1 and 2. The piping system and components were analyzed in accordance with the B31.3 piping codes. Approval was given to operate the system under pressure in the interim, based on the preliminary set of calculations. Some modifications were recommended and made based on the findings of the analysis, although no serious defects or code violations were found. The system proved to be fully capable of being operated at the design conditions identified for the various components.

The carbonizer vessel of the 100-lb/hr mild gasification unit was hydrostatically pressure-tested to 130 psi, with Twin City Testing serving as the independent observer to certify the testing procedures. Approval was given by the North Dakota state inspector to operate the carbonizer vessel under pressure. All piping modifications were completed, including the installation and pressure testing of new high-pressure/high-temperature valves.

### 3.1.4 Results of Testing Performed on the 100-lb/hr MGPDU

A computer model of the MGPDU was developed for use in determining the various gas flows necessary to meet the Foster-Wheeler test specifications for all matrix points. The model is interactive, calculating flow rates and expected products based upon the coal and dolomite feed rates, proximate and ultimate analyses of the coal, and run conditions. Due to heat losses, keeping the carbonizer at a reaction temperature of 1600°F requires that more coal be burned for heat than the 30% required by Foster-Wheeler. It was decided that additional heat could be supplied through the combustion of natural gas and a stoichiometric amount of air.

A test was performed in the pressurized carbonizer mode to determine the maximum flow rates possible for the various gas streams (purge N<sub>2</sub>, transport N<sub>2</sub>, O<sub>2</sub>, natural gas, the stoichiometric amount of air needed to burn the natural gas, and makeup N<sub>2</sub> needed to achieve the desired superficial velocity). The maximum flow rate information was compared with the various gas flow rates needed to successfully complete the experimental matrix. It was noted that some of the gas flow rates needed to complete the matrix were outside of the operational range of the equipment. To lower the gas flow rate

through the system, it was decided to use propane as the additional heat source rather than natural gas. The computer model was used to recalculate the gas flow rates necessary for the start-up sequence and test matrix using propane.

Following shakedown of the 100-lb/hr unit, five tests were performed. The operating conditions for these tests are given in Table 2.

#### 3.1.4.1 Run P016

Operation of the unit during Run P016 was consistent with design criteria until feed problems were encountered. Shortly after the feed problems developed, support instrumentation failure resulted in equipment dysfunction in the downstream quench train, producing another system upset. Further attempts to achieve steady-state operation were unproductive, and the test was terminated.

The problem with the feed system was determined to be contamination in the feed coal/dolomite mixture, and the problem with the quench train was satisfactorily resolved by instrumentation and control replacement.

#### 3.1.4.2 Run P017

Maintenance was performed on the unit, new feed material was prepared, and a second run was attempted. During this run, the unit operated very well at atmospheric conditions. A feed problem was encountered during stepwise sequential increases in pressure. At pressures over 30 psi, water condensation was noted in the pneumatic transport feed line. The water was noted in the drip leg below the transport zone. This condition apparently led to a plugged feed line. When the coal feed stopped, the internal temperature

TABLE 2

Operating Conditions of Tests Run in the 100-lb/hr MGPDU

Test Number	P106	P017	P018	P022-1	P022-2	P022-3
Coal	Wyodak <sup>a</sup>	Wyodak	Pitt.8 <sup>b</sup>	Wyodak	Wyodak	Pitt.8
Average Bed Temp., °F	900	1150	1650 <sup>c</sup>	1625	1625	1625
Pressure, psig	50-80	50-80	125	7	56	56
Coal Mix <sup>d</sup> Feed Rate, lb/hr	100	100	100	94	94	54.1 <sup>e</sup>
Coal Feed Size, inch	-¼ x 0	-¼ x 0	-¼ x 0	-¼ x 0	-¼ x 0	-¼ x 0
Dolomite Feed Size, mesh	8 x 16	8 x 16	-30	NA	NA	NA
Dolomite/Coal Ratio	15/85	15/85	30/70	23/77	23/77	23/77
Air Flow, scfh	3400	3400	3600	2200	3900	2900
Velocity, ft/sec	2-3	2-3	0.5-1	6.1	5.6	2.8

<sup>a</sup> Wyodak subbituminous coal.

<sup>b</sup> Pittsburgh No. 8 bituminous coal.

<sup>c</sup> Average value - temperature ranged from 1110° to 2190°F.

<sup>d</sup> Mixture of coal and Plum Run dolomite.

<sup>e</sup> Average value, feed rate increased during test period.

increased enough to cause bed sintering, terminating the run after approximately 20 hours of operation at a pressure of 90 psi.

In an effort to eliminate the coal feed difficulties, the function of the transport line during the pressurized carbonizer mode of operation was analyzed. Heat balance is difficult to maintain at this scale, and as a result, the gas-phase streams into the unit are heated. During mild gasification, a significant amount of the heat is supplied by the combustion of natural gas. In the pressurized carbonizer mode of operation, most of the heat is supplied by internal combustion. This means that, during operation, the air entering the system is essentially at room temperature. The transport tube passes through the natural gas combustion zone before entering the primary reactor. As the feed coal/dolomite mixture and preheated transport gas pass through the natural gas combustion zone, enough heat is lost to the incoming, room-temperature air to allow the condensation of a significant amount of either coal feed moisture or combustion moisture in the transport tube. This reduces the velocity of the transport nitrogen and disturbs its natural flow, causing agglomeration and plugging problems in the tube. It was decided that, prior to Run P018, minor equipment modifications and procedural changes would be adopted. The transport nitrogen feed line was modified to permit the use of air as well as nitrogen, meaning that room-temperature air could be used as the pneumatic transport gas. It was thought that this would eliminate the condensation problem and overcome a decrease in the net gas transport velocity during pressurization.

#### 3.1.4.3 Run P018

The equipment modifications suggested by the results of Run P017 were completed prior to the performance of Run P018. In addition, a sight port was added to the high-pressure burner. This enabled evaluation of a problem that had been experienced with lighting the burner at pressures over 30 psi. The sight port showed that the burner was lighting, but that the flame sensor was not "seeing" it. The sensor was moved, and the burner operated correctly.

The natural gas burner system had been modified and successfully operated at 1650°F and pressures up to 125 psi. The water quench system operated very well at pressures above 30 psi, preventing water from vaporizing in the first-stage system. The second-stage scrubber level instrumentation failed during heatup, but was monitored manually and did not present a problem. The electronic instrumentation for the coal transport velocity determination failed, and an operator took field readings to determine fluidization velocity. Due to the temperature loss caused by the introduction of a large amount of air, the transport gas was not introduced until shortly before the initiation of coal feed.

Within 10 minutes of the start of coal feed, large pressure fluctuations were noted in the bed and transport tube. Reactor temperature fluctuated from 1100° to 2190°F. Cycles between the temperature fluctuations occurred in a matter of minutes and were the result of inconsistent air flow to the reactor. All of the air was fed to the reactor through the transport tube. The tube plugged, diminishing the transport air flow and resulting in insufficient air to maintain reactor temperature. When the plug was blasted free, too much air entered the system. After approximately 1 hour, the feed system plug could not be blasted free, and the run was discontinued at that point.

Agglomerated coal was found at the bottom of the reactor, above the top of the char removal point. Clear passage was not evident at any point in the plug. It appears that the plug actually occurred in the main reactor and portions of the plug material fell to the bottom of the reactor and into the transport tube.

Table 3 presents the results of proximate/ultimate analyses of the feed coal, feed coal + dolomite, P018 char, and plug material from two locations. The data show that the agglomerates were enriched in ash relative to the feed coal/dolomite mixture. The agglomerate sample taken from near the bottom of the reactor contained more moisture and volatile matter than the agglomerate sample taken approximately 4 ft up the reactor. The agglomerates that were not found at the base of the reactor consisted almost entirely of fixed carbon and ash, indicating that this area experienced very high temperatures.

#### 3.1.4.4 Run P022

This run consisted of three test periods, designated P022-1 through P022-3. Agglomeration had been noted during earlier runs using Pittsburgh No. 8 bituminous coal; therefore, to ensure a successful system start-up, the run was initiated using Wyodak subbituminous coal, and the first test period consisted of operation using Wyodak coal at 7 psig (1.5 atm) and 1625°F. Char, condensate, and product gas samples were quantitatively taken during this test period.

TABLE 3

Results of Analysis of P018 Feed, Char, and Agglomerates

	Pitts 8 <sup>a</sup>	Coal/ Dolomite Mixture <sup>b</sup>	P018 Char	P018 Reactor Plug <sup>c</sup>	P018 Reactor Plug <sup>d</sup>
Proximate Analysis, wt% as-received					
Moisture	2.20	2.60	20.70	2.00	0.80
Volatile Matter	36.29	38.08	19.76	18.45	10.23
Fixed Carbon	50.30	39.20	30.16	20.78	43.57
Ash	11.20	20.11	29.37	58.75	45.39
Ultimate Analysis, wt% maf <sup>e</sup> basis					
H	5.34	5.18	1.64	2.48	0.70
C	81.33	81.06	82.81	85.29	99.47
N	1.56	1.36	1.10	1.40	1.56
S	3.76	3.17	3.42	6.07	5.03
O <sup>f</sup>	7.98	9.20	11.00	4.74	-6.77

<sup>a</sup> Pittsburgh No. 8 bituminous coal.

<sup>b</sup> Pittsburgh No. 8 and Plum Run dolomite.

<sup>c</sup> Located at the bottom of the reactor.

<sup>d</sup> Located 4 feet up the reactor.

<sup>e</sup> Moisture- and ash-free.

<sup>f</sup> Calculated by difference.

Once steady-state conditions were achieved during the first test period, the pressure was increased and the unit allowed to come to steady state again. The second test period consisted of operation of the unit on Wyodak coal at 1625°F and 56 psig (4.8 atm). Product gas samples were taken during this test period, but condensate and char samples were not.

When the pressure was maintained at 56 psig (4.8 atm) and the temperature at 1625°F, the feed was abruptly changed from Wyodak to Pittsburgh No. 8 coal. The coal/dolomite feed rate was increased over the course of the entire third run period, from 20 to 80 lb/hr. A hot spot developed on the side of the vessel where an unused nozzle had been insufficiently insulated, and the run was terminated. Following shutdown, no evidence existed of the extensive agglomeration of the Pittsburgh No. 8 coal that had occurred during the earlier attempts to carbonize it. A product gas sample was taken during the run period, and the char present in the cyclones and the char hopper at the end of the run was collected. A sample of the condensate was not taken during this run period.

The product gas samples that were collected during P022 were analyzed by gas chromatography. Char samples were analyzed for moisture, fixed carbon, volatile matter, and ash contents (proximate analysis); for C, H, N, S, and O (by difference) contents (ultimate analysis); and via x-ray fluorescence analysis to determine the inorganic constituents of the ash. The condensate was filtered and the solids subjected to determination of moisture, volatile matter, fixed carbon, ash, and sulfur contents; heating value; and solubility in tetrahydrofuran (THF). The condensate liquids were analyzed for total organic carbon and total phenolic contents. The density of the liquid fraction of the condensate was also determined.

A good mass balance could only be performed for the first run period due to the lack of quantitative samples. Because the data necessary to perform the mass balances were unavailable, the yield structure for the third run period (performed with Pittsburgh No. 8 coal) was determined in an alternate manner. The computer model of the mild gasification unit, that had been developed for use in determining the various gas flows necessary to meet the experimental matrix conditions, was modified to predict the product slate of carbonization. The model was originally developed using three steps:

1. Input of the flow rates and analyses of the feedstocks
2. Description of the chemical reactions occurring within the vessel with respect to the production of heat (i.e., burning methane and/or coal)
3. Performance of a heat balance over the system to obtain an estimate of the reactor heat loss

Additional information was added to the model so that it could be used to predict the yield structure of the carbonizer tests. The following information was incorporated during modification of the model:

4. Description of the chemical reactions taking place within the carbonizer



5. Development of chemical boundary machine constants based upon the behavior of the system during operation using Wyodak coal
6. Determination of the quantity of char produced
7. Determination of the quantity and speciation of product gases
8. Performance of mass and material balances on the system and the inclusion of this information in the model
9. Performance of an elemental balance over the vessel proper
10. Definition of the fourth reaction zone (in the water scrubber) and the reactions occurring there
11. Verification of mass, material, elemental, and heat balances for the entire system

### 3.1.5 Discussion of Results

Once completed, the model was used to predict the product slate of the first run period. This predicted product slate is compared to the actual product slate in Table 4. As the table shows, the model accurately predicts

TABLE 4  
Comparison of Predicted P022 Run Period 1 Product  
Slate with Actual Product Slate<sup>a</sup>

Coal:	Wyodak	
	Predicted	Actual
Product Gas, lb		
O <sub>2</sub>	66	21
H <sub>2</sub>	30	30
CO <sub>2</sub>	617	577
N <sub>2</sub>	1355	1430
CO	410	402
CH <sub>4</sub>	27	22
H <sub>2</sub> O	5.5	5.6
Total	2510.5	2487.6
Condensate, lb	322	294
Char (maf <sup>b</sup> ), lb	62	62
Dolomite + Ash, lb	110	91
Water in Char, lb	4.9	4.7
Closure	100%	98.14%
Char Yield	13.8%	11.2%

<sup>a</sup> Total quantities produced during run period with Wyodak coal.

<sup>b</sup> Moisture- and ash-free.

the product slate for the run period using Wyodak subbituminous coal. There is little reason to expect that it could not also be successfully used to predict the product slate of the carbonization of Pittsburgh No. 8 bituminous coal.

Table 5 compares the predicted product slate for run period 3 with the actual product slate (such as could be calculated) from the Pittsburgh No. 8 run period. Not all values could be compared due to the lack of samples, but the predicted and actual gas product slates agree fairly well. The char samples collected during this run period were taken from the char hopper and the cyclones. The ultimate analysis of the char in the char hopper was quite different from that of the cyclone fines, as can be seen in Table 6. Based

TABLE 5  
Comparison of Predicted P022 Run Period 3 Product  
Slate with Actual Product Slate<sup>a</sup>

Coal:	Predicted	Actual	
	Pittsburgh #8	Pittsburgh #8	
Product Gas, lb			
O <sub>2</sub>	21	5	
H <sub>2</sub>	6	3	
CO <sub>2</sub>	175	119	
N <sub>2</sub>	686	750	
CO	45	37	
CH <sub>4</sub>	12	8	
H <sub>2</sub> O	6.6	-- <sup>b</sup>	
Total	951.6	--	
Condensate, lb	26.4	--	
Char (maf <sup>c</sup> ), lb	22.5	--	
Dolomite + Ash, lb	25.5	--	
Water in Char, lb	0.2	--	
Char Analysis, wt% maf coal			
H	3.14	0.67	Weighted average of all analyses <sup>e</sup>
C	72.31	72.04	
N	2.17	0.98	
S	10.48	3.34	
O <sup>d</sup>	11.91	22.96	
Closure	99%	--	
Char Yield	25.6%		

<sup>a</sup> Total quantities produced during run period with Pittsburgh No. 8 coal.

<sup>b</sup> Information not available.

<sup>c</sup> Moisture- and ash-free.

<sup>d</sup> By difference.

<sup>e</sup> Ranges of analyses are given in Table 6.

TABLE 6  
Elemental Analysis of Char and Cyclone Fines  
from P022 Run Period 3<sup>a</sup>

	Char Hopper	Cyclone Fines
H	0.91	0.54
C	90.10	62.99
N	1.37	0.76
S	9.29	0.05
O <sup>b</sup>	-1.69	35.64

<sup>a</sup> All values in wt% on a moisture- and ash-free basis.

<sup>b</sup> By difference.

upon the quantities collected from each location during the Wyodak run period, these values were weighted to arrive at an average char analysis, which is shown in Table 5. The predicted and average values agree fairly well when it is taken into account that small real differences at this scale can result in dramatically different percentages. It should also be noted that most of the predicted values fall within the range defined by the two char analyses.

Based upon the product slate predicted using the computer model, it appears that operation at 1625°F, 4.8 atm, and the gas flow rates noted in Table 1 results in a char yield of approximately 25 wt% of the Pittsburgh No. 8 coal fed to the system.

### 3.2 Fate of Alkali in PFBC Systems

Data from turbine-operating experience using residual oil and from PFBC experiments indicate that alkali metal compounds play a large role in the amount of deposition and hot corrosion experienced by turbomachinery (1). If pressurized fluidized-bed combustion is ever to become a commercial reality, an understanding of the extent of alkali metal compound emissions from the combustor, its effect on the turbine, and ways for controlling these emissions is needed.

Sodium and potassium compounds exist in the coal in similar chemical forms. Sodium and potassium are constituents of clay minerals; NaCl is present in the coal bed moisture and as a discrete mineral in the coal. While KCl is also found in the groundwater, potassium is present in the coal largely as nonvolatile aluminosilicates. The potassium can then be released from the silicates as KCl through an exchange reaction with NaCl vapor. Both NaCl and KCl have significant vapor pressures at 900°C (3.0- and 5.3-mmHg, respectively), so their vapor is expected in the PFBC flue gas.

Researchers at Westinghouse concluded, based on thermodynamic modeling, that the release of sodium increases with increasing temperature, increasing chlorine content of the fuel, and decreasing SO<sub>2</sub> levels in the gas and decreases with increasing pressure (1). These studies also indicated that the major sodium and potassium species evolved should be NaCl and KCl; however, alkali metal sulfates can result from the reaction of the chlorides with gaseous sulfur compounds.

### 3.2.1 Measurement Techniques

One concern in understanding the fate of alkali in a PFBC system is the ability to measure the amount of alkali volatilized under these conditions. Several techniques have been developed to measure the alkali levels in flue gases. These techniques include in situ techniques such as laser-induced fluorescence spectroscopy (LIFS); laser-induced photo and fluorescence (LIPF); laser-induced breakdown spectroscopy (LIBS); hot-extraction techniques, such as the Ames alkali monitor and the METC Fiber Optic Alkali Monitor (FOAM) analyzer; and a batch-type, condensation cold trap such as the alkali and particulate sampling train (APST) technique. One additional technique is the use of a fixed bed of alkali sorbent material in which a known amount of flue gas is passed through the bed for a given time, after which the bed material is regenerated and analyzed for its alkali content.

The EERC has performed some testing using a LIFS system to look at the concentration of Na atoms in a small-scale burner (2). These tests looked at sodium in solution, solid-phase sodium compounds, sodium impregnated on carbon, and three different Beulah lignite coal samples. These samples were a demineralized Beulah lignite, a demineralized Beulah lignite with sodium acetate impregnated back into the sample, and a raw Beulah lignite. The form of the sodium in solution was found to have no effect on the concentrations measured. The solid-phase sodium salts (benzoate, sulfate, and carbonate) gave signals similar to the solutions, while the sodium montmorillonite and chloride gave signals much less than those observed for solutions. The coal and char samples gave signals higher than the solutions, and there was a linear response of the coal samples with Na concentration in the sample. Solgasmix, a thermodynamic code for predicting the equilibrium composition of various inorganics in high-temperature environments, was used to predict how much Na would be in the atomic state. The code did agree with the general observations that NaCl and sodium montmorillonite liberated less Na when combusted; however, the predictions were 30% to 70% in error since the mole fraction values put into the program were that much in error.

Los Alamos National Laboratory has performed some laboratory testing with a photofragment fluorescence technique which is capable of identifying different anions of the same alkali (3). This technique is based on the UV laser-induced photodissociation of alkali-containing compounds. Sodium and potassium compounds can be distinguished by their characteristic emission wavelength (589 nm for Na<sup>+</sup>, 766 nm for K<sup>+</sup>). Variation of the threshold energy wavelength should allow good discrimination between alkali compounds with different anion groups. Research indicates that the instrument is sensitive down to 0.03-ppb NaCl and 0.4-ppb KCl, 0.1-ppb NaOH and 7-ppb KOH, and 0.01-ppb Na<sub>2</sub>SO<sub>4</sub> and 0.3-ppb K<sub>2</sub>SO<sub>4</sub>. This research concluded that, in predominately binary mixtures of the chloride anion with the hydroxide or sulfate anion, the photofragment fluorescence technique will be able to distinguish the concentration of each compound. However, in mixtures containing comparable amounts of the hydroxide and sulfate anions, the spectra are similar enough to make concentration measurements difficult. Research with the photodissociation fluorescence technique is being continued at PSI Technologies, Co., in testing on their laminar flow drop-tube furnace (4). Results have been obtained which indicate that chlorine is the species-limiting compound in the formation of NaCl. Solgasmix was used to validate the dependence of NaCl formation on the chlorine levels in the coal.

Additional kinetic modeling was performed to determine that the NaCl equilibrium is approached in approximately 5 ms.

Work at Argonne National Lab (ANL) has compared the Ames alkali monitor, the METC FOAM analyzer, an APST condensation technique, and the alkali sorbent bed (5-9). Their results indicate that hot-extraction techniques result in considerable condensation of alkali on the heated sample lines, even at temperatures up to 950°C. The Na concentrations were found to be approximately 0.1 to 0.3 ppm with this technique. The APST batch-type condensation train gives alkali levels between 0.6- and 1.0-ppm Na, while the sorbent bed gives values between 1.3- and 1.5-ppm Na, which is 15 times higher than the current industrial gas turbine limit of 0.024 ppm of alkali. The discrepancies in the numbers have been attributed to the absorption of the alkali on the heated sample lines, while the sorbent bed is right in the flow gas, so there is no sample line to change the concentrations. The sorbent bed numbers could be inflated due to some contamination by particulate.

Thermodynamic equilibrium studies have been conducted at the EERC using the Solgasmix and PHOEBE codes. Solgasmix is a free energy minimization code developed by Eriksson (10). PHOEBE is a Gibbs free energy minimization program developed at the EERC by Ramanathan, Kalmanovitch, and Ness (11, 12). Solgasmix was tested extensively in-house and appeared to perform adequately, although the occasional output of erroneous results was discovered. PHOEBE was found to perform better than Solgasmix in calculations on the binary  $Al_2O_3:SiO_2$  system and the  $Na_2O:Al_2O_3:SiO_2$  ternary systems. PHOEBE was in very good agreement with the binary system and showed some interchange between the primary and secondary (or secondary and tertiary) phases in the predicted values.

A review of the literature being used to design the carbonizer for the Foster Wheeler second-generation PFBC system indicates that the dry tar had ash levels ranging from 0.1 to 3.2 wt% ash (avg. 1.0 wt%) (13). While some of the ash could be the result of fine fly ash carrying over out of the carbonizer, some of the ash is probably due to the volatilization of alkali metal compounds which would not be collectible by a hot-gas cleanup device such as ceramic candle filters, etc. The presence of organic vapors in the gas stream will also make the sampling and identification of alkali compounds more difficult. The organic vapors are known to absorb UV radiation which will preclude the use of any laser-induced fluorescence technique because they fluoresce in the UV wavelengths. Condensation cold-trap sampling trains would also condense the organic tars, making the analyses for alkali compounds much more difficult. A fixed bed of sorbent material could potentially work as an alkali measurement device, provided the bed is maintained at the same temperature as the gas/tar stream to prevent the condensation of tars on the sorbent material.

### 3.2.2 Alkali Evolution under Reducing Conditions

Alkali sampling from the Texaco slagging gasifier has been reported by Haas and others (14) using the METC/Idaho National Engineering Laboratory (INEL) fiber optic alkali meter. This sampling was conducted at 650° to 700°C and 365 psia. The observed alkali concentrations were 10 to 20 ppbw for each of both sodium and potassium using a Pittsburgh #8 bituminous coal. These concentrations were comparable to alkali concentrations measured from a PFBC

system at the Argonne National Laboratory (30 to 40 ppbw Na and 10 to 30 ppbw K).

A study by Greene and others (15) used a molecular beam mass spectrometer (MBMS) system mounted on a well-characterized coal reactor. Results from this study indicate that the sodium is volatilized from the coal particle during the coal devolatilization step and occurs, principally, as the atomic species rather than as the oxide or hydroxide. This sodium is quickly converted to an unknown gaseous species or a condensed phase such as a fume. High initial concentrations have been detected in the vicinity of the coal particle (<1 mm) with concentrations exceeding 700-ppm maximum and averaging >100 ppm. These concentrations are not representative of the alkali concentration in the final flue gas; however, these data can be used to calculate fluxes of alkali away from the coal particle as a function of time. It should be noted that data indicate that less sodium was volatilized under simulated gasification operating conditions than under simulated PFBC operating conditions. This surprising result could be the result of higher particle temperatures being achieved under the simulation of PFBC operating conditions than under the simulated gasification operating conditions. Another possibility was that less of the alkali was volatilized as an atomic species, but was volatilized as a chloride species which was not subject to analysis.

Knudsen cell mass spectroscopy work on low-temperature ashed samples of Illinois #6 and Wyodak coals was conducted by SRI International (16). In the work with the Wyodak subbituminous coal, NaCl and KCl were observed as vapor species above the coal ash, but these species were not detected above the Illinois #6 coal ash. The chlorine levels in the Wyodak were approximately three times higher than in the Illinois #6 sample. The previously unobserved species  $\text{NaBS}_2$  and  $\text{KBS}_2$  were identified above both the Illinois #6 and Wyodak coal ash samples. This study indicated that the vapor pressure of atomic species decreased substantially with increasing  $\text{O}_2$  concentration in the gas, and the other alkali species decreased slightly with increasing  $\text{O}_2$ , except for the hydroxide species which showed an increasing concentration with increasing oxygen. This work also indicated that at the 800° to 900°C operating temperature range for our carbonizer testing, the chlorides would have the highest vapor concentrations under gasification operating conditions. The concentration of the alkali chlorides was either not found or found in concentrations less than that predicted with a thermochemical equilibrium code. Some preliminary thermochemical equilibrium calculations indicate that in-bed desulfurization may enhance alkali vaporization due to the replacement of alkali by alkaline earth elements in stable aluminosilicate phases in the ash.

Thermochemical equilibrium calculations performed on the combustion and gasification of peat indicate that, under reducing conditions, the concentrations of vapor-phase alkali are approximately two orders of magnitude higher than that under the PFBC operating conditions (17, 18). The sodium and potassium concentrations in the product gas under PFB gasification conditions ranged from 7.5 ppm at 700°C to 76.2 ppm at 900°C, while the sodium and potassium concentrations in the PFBC flue gas ranged from 0.05 ppm at 800°C to 5.9 ppm at 1000°C. The concentration of the vapor-phase alkali was strongly dependent on the operating temperature and pressure. An increase in operating temperature from 800° to 900°C in the PFBC environment increased the vapor-phase alkali metal concentrations approximately one order of magnitude.

However, an increase in operating temperature in the gasification environment increased the vapor-phase alkali metal concentration approximately 70%. An increase in pressure from 1 to 10 bar was calculated to decrease the concentration of alkali metals by approximately one order of magnitude in the temperature range from 800° to 900°C under PFBC operating conditions. An increase in operating pressure from 1 to 10 bar was calculated to produce a less than a twofold decrease in alkali concentration in the same temperature range under gasification operating conditions. A strong dependence on the chlorine content was also calculated, with higher concentrations of vapor-phase alkali metals occurring with higher concentrations of chlorine in the fuel. Under PFBC operating conditions, the gas phase was calculated to contain alkali chlorides and to a lesser extent hydroxides with some  $\text{Na}_2\text{SO}_4$  also present at higher temperatures. All of the volatilized alkali species show a steady but small increase in concentration with an increase in the alkali content of the fuel. The liquid phase consists principally of the alkali sulfates.

Under gasification operating conditions, the volatilized alkali metals consist primarily of chloride and hydroxide compounds, with dichlorides and atomic alkali compounds also being present at lower concentrations than the monochlorides. The hydroxide concentration in the gasification product gas shows a steady or slightly increasing concentration with increasing alkali levels in the fuel, while the chloride concentration shows a decrease with increasing alkali level. The liquid phase consists of chlorides and carbonates, with the chloride concentration being one order of magnitude higher than the carbonates.

These thermochemical equilibrium data were compared to experimental data collected from a pressurized fluid-bed unit which can be run in both the combustion and gasification mode. At a bed temperature of 840°C in the PFBC mode, approximately 0.3% of the potassium and 1.4% of the sodium were volatilized in the bed, resulting in an alkali concentration of approximately 1.1 ppmw. This concentration is significantly higher than the thermochemical equilibrium calculations would indicate.

At a bed temperature of approximately 830°C and a freeboard temperature of approximately 860°C in gasification modes, the sodium concentration ranged from 2.1 to 4.3 ppmw, while the potassium ranged from 0.8 to 1.1 ppmw. This corresponds to 2.4% to 4.6% of the sodium and 0.7% to 1.1% of the potassium being volatilized. The sodium concentrations are slightly less than those calculated, while the potassium concentration is significantly less than that calculated in the thermochemical equilibrium code. While the ash chemistry of peat is probably significantly different than that of coal, the general trends displayed in this study are still expected to be true.

The current data indicate that the concentration of volatilized alkali metal species should be higher for a given coal under the reducing conditions of the carbonizer than the oxidizing conditions of the circulating PFBC system. The presence of approximately 0.08 wt% chlorine in the Pittsburgh #8 test coal suggests that alkali chlorides will be present in significant quantities, especially in the carbonizer product gas.

### 3.2.3 Alkali Getters

Alkali released during PFBC applications and present in the vapor phase in the flue gas has been measured in the range of 0.1 to 10 ppmw (19-21). This is considerably higher than the 0.024 ppmw recommended by turbine manufacturers, even though it represents only about 1% to 2% of the total alkali in the coal. Therefore, some form of alkali removal is required.

A number of researchers and developers have been working with various alkali getters to remove alkali from the hot-gas stream. Since contacting the alkali with the getter is critical, various packed-bed and granular-bed filters have been used. Westinghouse (22, 23), Argonne National Laboratory (19, 24, 25), and the Coal Research Establishment (26) have all looked at alkali getters in a packed bed, while the work done at Combustion Power Company (CPC) (27, 28) and New York University (NYU) (20, 29) utilized a granular-bed filter (GBF) design. The University of Arizona considered using the getter in situ with the combustion or gasification process (21, 30). At least 13 different potential alkali getters have been tested by these various institutions. The three most successful getters tested have been bauxite, kaolinite, and emathlite. Alkali is captured by bauxite primarily by physical adsorption. Some chemical fixation by the clay impurities also occurs. Bauxite has been tested as an alkali getter at temperatures ranging from 1350° to 1850°F. The apparent activation energy for the bauxite was low, indicating that temperature has only a small impact on its ability to adsorb alkali. In contrast, kaolinite and emathlite remove alkali by chemical reaction of the sodium and potassium with these silicate-based minerals. Kaolinite has a high activation energy, indicating it is sensitive to temperature, with alkali removal increasing with increasing temperature. Emathlite had a small activation energy, indicating its relative insensitivity to temperature.

The maximum temperature limitations will differ for these three getters. The emathlite reacts with the sodium to form albite, a sodium aluminosilicate compound. Albite has a melting temperature of 1832°F. At temperatures above 1832°F, a glass will form which could potentially cause sticking and agglomerating problems within the bed. Kaolinite, on the other hand, will form nephelite and/or carnegieite, depending upon the temperature of the bed. The relative melting point of nephelite, which is the favored species at higher temperatures, is 2840°F. If a granular bed of nephelite proves to be an effective alkali getter and particulate removal device, it would have the distinct advantage of operating at combustor exit temperatures, eliminating the costly steps of cooling, cleaning, and reheating the flue gas. Bauxite will not melt until 3600°F; however, its adsorption capacity will decrease as the temperature increases.

Preliminary kinetic analysis of alkali capture rates with alumina silicate (such as bauxite) additives indicate that, in the 1500° to 2000°C region, alkali capture rates are 100 times faster than the similar kinetic capture process found with sulfur and calcium oxide (31). Activated bauxite has been found to be twice as effective as diatomaceous earth at removing alkali vapors from gas streams (5, 9). Alkali gettering is best achieved by passing the products of combustion (POC) through a packed bed of activated bauxite pellets. Greater than 99.9% removal of NaCl vapor has been achieved in a simulated PFBC flue gas at 800°C, 5 atm, 3.4% water vapor, but with no SO<sub>2</sub>. The NaCl was found to have reacted with the bauxite to form water-



soluble sodium meta-aluminate. In contrast, the NaCl vapor in the same simulated PFBC flue gas with SO<sub>2</sub> was captured as a condensed-phase sodium sulfate. The sodium sulfate could either be formed as aerosols in the gas phase and captured by the bauxite bed, or the sodium sulfate could be formed over the surface of the bauxite through a heterogeneously catalyzed reaction (9). Due to the high predicted capture rates, the direct injection of alumina silicate additives into the combustor should also be very effective (31); however, the alkali-saturated sorbent tends to be sticky. This stickiness probably will present problems for hot-gas cleanup devices such as ceramic cross-flow filters and cyclones; however, further research is needed to determine the significance of this problem.

Pilot-scale tests have been performed by ANL on their pilot-scale PFBC using bauxite as an alkali getter (19, 24, 25). Tests were performed at 1560° and 1610°F using a lignite from Beulah, North Dakota. Flue gas concentrations of 1.4- to 1.5-ppmw sodium and 0.1-ppmw potassium were measured at the inlet to the filter device. Using a packed bed of bauxite with a particle size ranging from 2 to 2.4 mm effected greater than 99% removal of the alkali. The outlet alkali measurements were less than 10 ppbw. Adsorption data were collected that can be used for preliminary design scaleup.

The CPC GBF was tested at NYU using Beulah lignite with 8.0% ash and 0.62% sodium (as Na<sub>2</sub>O) in the coal as the fuel (20, 29). The PFBC pilot plant was operated at temperatures ranging from 1490° to 1600°F and 6.9 to 9.2 atmospheres. Both 2- and 3-mm mullite particles were tested. The average alkali content in the flue gas entering the GBF was measured to be 1.25% of the sodium and 1.12% of the potassium in the coal. The measured alkali-gettering efficiency for all of the tests was between 90% and 96%, with a possible error of 5%. The outlet alkali concentration ranged from 3 to 20 ppbw, which is below the 24-ppmw recommended turbine tolerance limit. In this work, no attempt was made to determine the mechanism of capture, i.e., whether the alkali reduction was due to condensation on the filter media, capture of fine alkali sulfate dust and aerosol particles, physical adsorption, or chemical absorption and reaction. Therefore, although it was proven that the concept will simultaneously capture particulate and alkali, no scaleup data were obtained.

A more practical study was performed by Westinghouse, focusing on emathlite as the getter material (22). Results from the testing indicated that the concept of using a fixed bed of emathlite pellets is a practical technique for alkali removal from hot flue gases. Process development tests included a 102-hour test where gas containing 10-ppmv NaCl was reduced to less than 0.2 ppmv (detection limits). In other studies, alkali removal of greater than 99% was demonstrated, with a reduction of sodium to below the 20-ppb turbine tolerance level. A commercialized process has been identified for manufacture of the emathlite pellets. In that testing, the kinetics were found to be insensitive to temperature over the range of 1426° to 1651°F. The absorption rate was proportional to the alkali gas-phase concentration, with no capacity limitations due to absorption limitation at low gas-phase alkali concentrations. The Westinghouse research was based on a packed-bed design, and it was felt that it would be necessary to install a particulate cleanup device ahead of the sorbent bed. Westinghouse had envisioned a long time between replacement of the bed material (one-half to one year) and had concerns about bed pluggage due to the fly ash. The use of a GBF would

preclude this from happening. An important finding from the Westinghouse work was that no attrition of the emathlite pellets was noted during any of the testing. Recommendations were to use 6-mm pellets for the packed bed.

All of these studies have been performed using combustion gases. In a combustion atmosphere, most of the alkali material is vaporized during combustion and will be present as a sulfate. At the typical filter temperatures (1450° to 1650°F), a majority of the sulfates will have condensed on the surface of other ash particles, or as fine particles and aerosols (26, 32, 33). The removal of the alkali in this form is difficult because of the need to capture the fine sulfate particles and either remove them as sulfates or provide the contact necessary to react the sulfates with the getter material. The good performance results by ANL, NYU, and Westinghouse indicated this is possible.

Less testing has been done for gasification systems. Thermodynamic calculations for a reducing atmosphere indicate that the alkali will be present as hydroxide vapors or chloride vapors for high-chlorine coals.

The effect of chlorine on the performance of alkali getters has been reported by Singh and others (34) under both PFBC and gasification conditions. Under both sets of operating conditions, the presence of HCl in the flue gas is expected to decrease the getter efficiency, although gasification operating conditions seem to be more significantly affected. Increasing pressure and decreasing temperature also seem to improve the getter efficiency. Potential getter reactions for alkali chloride compounds all form HCl in the product gas; therefore, if there is a high HCl concentration in the product gas, it limits the gettering reaction due to the thermochemical equilibrium. Methods for the removal of HCl were studied (35), but they used a Na<sub>2</sub>CO<sub>3</sub>-based mineral at lower operating temperatures (535°-650°C).

Work from previous researchers has demonstrated that alkali getters can be effective in removing alkali from both combustion and gasification gas streams. Both packed-bed and granular-bed filters have been utilized. Drawbacks include the need for a particulate removal device both before and after a packed bed and the expense of the added pressure vessels to contain the packed or granular bed. The granular bed may be cost-effective if both particulate and alkali control can be achieved. However, because of the disadvantages associated with packed and granular beds, in situ removal of alkali may be preferred. A getter, used in the same manner as a sorbent is used to remove sulfur, would not add any significant cost to the system, would be easy to maintain, and could be used in both oxidizing and reducing atmospheres. During the next program year, the EERC will continue to pursue the use of in situ alkali getters for second-generation systems.

### **3.3 Bench-Scale Reactor Testing**

#### **3.3.1 Bench-Scale Reactor Design**

As discussed during the project review meeting at METC in August 1990, the EERC had planned to make use of an existing bench-scale reactor as a pressurized fluid-bed reactor (PFBR). As design efforts proceeded, the number of limitations imposed on the PFBR design by using the existing equipment kept increasing. These limitations included reactor height and diameter, coal and

sorbent feed options, air preheat capabilities, and the amount of heat duty the reactor could handle. Therefore, it was decided that a stand-alone reactor should be designed to ensure that the reactor could meet all of the objectives of this project.

The pressurized fluidized-bed reactor has been designed and is being constructed to allow extensive alkali and hot-gas cleanup testing on a cost-effective manner over a wide range of operational conditions. Preheated fluidizing gas at temperatures up to 1000°F and pressures up to 150 psig will be supplied at the bottom of the reactor through a 1-in Schedule 40 pipe at sufficiently high velocities to prevent the sized bed material from dropping out during operation. Bed material can be sampled or collected using a lock hopper system located at the bottom of the reactor. The fluidizing gas enters into the 3-in Schedule 80 main section of the reactor through a conical transition. The operating velocities in the 3-in section will allow some internal recirculation of the fluidized-bed material. External heaters will be used for heating and maintaining the reactor and hot cyclone at temperatures up to 2000°F for atmospheric operation and up to 1700°F for operation at 150 psig.

Limestone, inert bed material, or ash generated from a combustor or by an ashing procedure can be added at the start of a test using a lock hopper system. Selected additives and coal can be fed separately at controlled rates during testing. Coal feed, when utilized, will be maintained at a low rate to eliminate any heat removal requirements from the reactor. Fluidizing gas can be supplied as air or as various mixtures of nitrogen, oxygen, carbon dioxide, carbon monoxide, sulfur dioxide, and nitrogen oxides to result in a flue gas similar to that generated in a full-scale fluidized-bed boiler. Different oxidizing and reducing condition tests can also be conducted. An alkali sampling probe can be inserted through the top of the reactor or through the top of the hot cyclone for when hot-gas cleanup testing is being conducted.

A data acquisition/control system will be used to monitor and record all critical pressures, temperatures, and flows and to remotely control the numerous valves distributed throughout the system. All high-pressure feed and collection hoppers will be monitored with pressure transmitters. A solids-sampling port and a gas-sampling port will be at the top of the combustor.

### 3.3.2 Sulfur Retention Efficiency

The sulfur retention efficiency in the combustor is influenced by many factors, including gas and solids residence times in the bed and freeboard, bed temperature, reactivity of the sorbent, particle size, and oxygen concentration at the bottom of the bed. Within the range of operating conditions of PFBC, the sulfur retention increases with increased bed temperature, Ca/S molar ratio, and gas residence times.

In a PFBC, limestone is less effective than dolomite in removing SO<sub>2</sub> on the basis of Ca/S molar ratio. A probable explanation is that a prerequisite of good sulfur retention efficiency is the development of porosity in the sorbent particles. With limestones, porosity is developed due to calcination which occurs readily at atmospheric pressure, but with greater difficulty in a pressurized system because the partial pressure of CO<sub>2</sub> corresponding to high pressure in the bed is higher than the equilibrium partial pressure of CO<sub>2</sub> for

CaCO<sub>3</sub>. As a result of the difficulty in achieving calcination of limestone at high pressure, the effectiveness of limestones is reduced. Dolomite is about twice as effective as limestone, and 90% sulfur retention efficiency can be expected with dolomite with a Ca/S molar ratio of 1.5 under typical PFBC operating conditions.

The sulfur retention efficiency can be improved for bubbling-bed PFBCs at the expense of process efficiency by a) employing low fluidizing velocity which requires a smaller bed particle size, b) using deep beds and hence longer residence time, and c) recycling fines captured by the primary cyclones. It can also be improved by as much as 30% by using two-stage combustion.

Although dolomite does provide a porous sorbent for PFBC operation, it is still very probable that limestone would be a preferable sorbent selection for use in any PFBC system, based upon results obtained at Grimethorpe (36). Because limestone has a higher CaCO<sub>3</sub> content and because the Mg component of dolomite does not react with SO<sub>2</sub>, limestone can be as efficient as dolomite in a PFBC system when a sorbent/sulfur mass ratio basis is utilized. It is the mass ratio that will ultimately determine the sorbent requirements and output solids disposal in practical and economic terms.

Based on tests carried out in a small combustor, correlations have been proposed for sulfur capture and can be used with reasonable accuracy to estimate the performance of a sorbent in a large combustor. One such correlation, proposed by the International Energy Agency (IEA) group (36), is:

$$R = 100 (1 - \exp(-MC)) \quad [\text{Eq. 1}]$$

where R is the sulfur-removal efficiency; C is the molar ratio of calcium in the sorbent to sulfur in the fuel fed; and M is a parameter dependent on sorbent properties and operating conditions, principally bed height, fluidizing velocity, and bed temperature. The parameter M is given by the following correlation:

$$M = A t^{1/2} \exp(4600/T) \quad [\text{Eq. 2}]$$

where t (= H/V) is gas residence time, H is the bed height, V is the fluidizing velocity, T is the bed temperature, and A is a reactivity index (A = 38 and 50 for Whitewall and Plum Run dolomites, respectively).

However, for a reliable estimate of the sulfur retention by either dolomite or limestone added to the bed, one still must rely heavily upon experimental work carried out under operating conditions closely approximating those that will apply in a commercial plant. It is also expected that operation in a circulating mode will greatly enhance sorbent utilization, and that any predictive equations proposed should be modified to account for the operating characteristics of the circulating bed.

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**APPENDIX A:**

**UND ENERGY AND ENVIRONMENTAL RESEARCH CENTER  
100-LB/HR MILD GASIFICATION PROCESS DEVELOPMENT UNIT (MGPDU) DESCRIPTION**



Task 4, which includes the 100-lb/hr MGPDU, was initiated in November 1988. This task includes 1) the design, construction, and operation of the PDU; 2) product analysis and upgrading studies, some of which will be performed under subcontracts; and 3) a technical and economic evaluation leading to a decision on further scaleup to a 1-ton/hr pilot plant and a subsequent demonstration plant. The MGPDU will serve two principal purposes in the development of this technology: 1) provide proof of concept for an integrated design operating on specific design coals, and 2) produce char and liquid products for upgrade testing and market evaluation.

## PROCESSING CAPABILITIES

The MGPDU has been designed to process 100 lb/hr of feed coal (dry basis). The system incorporates capabilities for drying, carbonizing, and calcining caking and noncaking coals in fluid-bed reactors and for separating char, liquid, and gaseous products. The system is designed for integrated operation, and provisions have been made so carbonizing can take place without having to utilize the calciner.

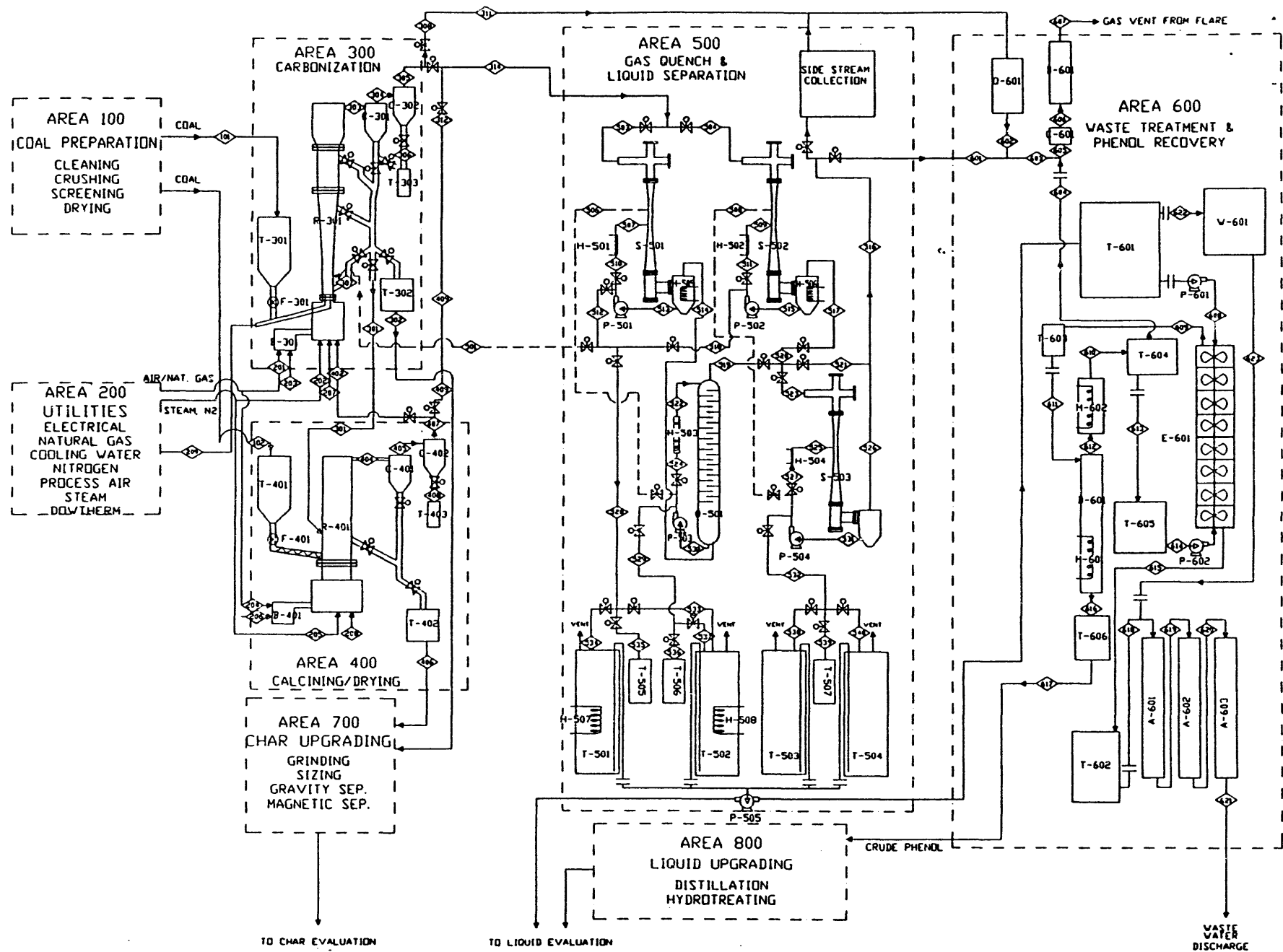
Heat for carbonization and for the calciner are principally supplied by hot flue gas from stoichiometric combustion of natural gas, or, in a later commercial design, by combustion of process-derived gas and waste coal from coal cleaning in a fluid-bed combustor. Combustion is external to the gasification reactors and is air-blown to avoid the cost of an oxygen plant in the commercial design. Provisions for steam injection have been made because of the sulfur removal effects of the steam and the increase in liquid quality, as seen under Task 2. High-temperature steam can also be employed in the calciner for the production of activated carbon, or to increase the H<sub>2</sub> and CO content of the gas passed from the calciner to the carbonizer during integrated operation.

## FLOW SHEET AND PROCESS DESCRIPTION

The flow sheet shown in Figure A1 is subdivided into eight sections which have been used as the basis for organizing the detailed design. The subsequent section on nomenclature contains the letter codes, area codes, and individual unit names. Table 1 indicates the general area designations.

### Area 100 - Coal Preparation

Illinois No. 6 and Indiana No. 3 feed coals may be washed at the mine and are crushed and screened at the EERC to a typical size of 1/4 inch by 0. The Wyoming feed coal is screened to a similar size, but is not washed. The option of drying the feed coal before it is fed to the carbonizer is a test variable. The main purpose for drying is to limit the moisture entering the gasification train in tests at low-steam input to the carbonizer so as to reduce or eliminate the net production of wastewater condensate. Moisture reduction is performed in a nonintegrated mode using a roto louver dryer available at the EERC. If lower moisture contents are desired, the coal can be further dried at low temperature (<570°F/300°C) in the carbonizer.



A-2

Figure A1. Flow sheet for EERC 100-lb/hr process development unit.

TABLE A1

## Area Descriptions

<u>Area</u>	<u>Name</u>
100	Coal Preparation
200	Utilities
300	Carbonization
400	Calcining
500	Gas Quench & Liquid Separation
600	Waste Treatment & Phenol Recovery
700	Char Upgrading
800	Liquid Upgrading

**Area 200 - Utilities**

Utilities that are necessary include 1) electrical services, 2) natural gas, 3) cooling water, 4) nitrogen, 5) process air, 6) steam boiler and superheater, and 7) a high-temperature heating/cooling system. In addition, a contingency design has been developed for refrigerated cooling for a light-oil condenser, if needed. All utilities were in existence except the steam boiler and superheater, the high-temperature heating/cooling system, and the refrigerated cooler contingency. The heating/cooling system is capable of operating at elevated temperatures in order to cool the tar that is recirculated to the tar venturi scrubber. This system is necessary in order to avoid low metal temperatures that would cause "freezing" of tar on the heat-transfer surface. In the other scrubber heat exchangers, cooling water is used.

**Area 300 - Carbonization**

The carbonizer is designed as a spouted-bed gasifier, based on favorable results with caking coals in the COALCON and KRW gasifier systems. The operative principle allowing use of caking coal in this design is the dilution of the entering coal by an internal recycle of char to the bottom of the tapered bed, where high velocity and low bed density also reduce agglomeration. A similar regime existed in the 400-lb/hr fast fluid-bed Perry carbonizer previously used on caking coals at the EERC. In the event that agglomeration problems are encountered in the MGPDU operating on Indiana No. 3 feed coal, product char from the char receiver will be fed into the bottom of the gasifier to augment internal char dilution. Still another means for controlling agglomeration that may be applicable to this design involves the use of a coarse sand bed in the high-velocity section, as employed by CSIRO in Australia. Successful use of this technique would require segregation of the coarse sand in the high-velocity section to avoid contamination of the char withdrawn from the top of the bed in a low-velocity region. Char residence time can be varied by bed height, with the base design being 30 minutes.

The carbonizer operates at temperatures from 900° to 1110°F (480° to 600°C) with steam partial pressures from 10% to 60%. During integrated operation, the carbonizer receives hot gas from the calciner; depending on the atmosphere and resulting gasification reaction in the calciner, this gas can

be made to contain significant levels of H<sub>2</sub> and CO reductant to assist in sulfur removal. The coal is entrained and fed into the bottom of the reactor using preheated nitrogen (575°F/300°C). Char can be drawn from a variety of locations and injected into the calciner or the tote bin, or reinjected into the system.

#### **Area 400 - Calcining**

The calcining reactor is a modification of the bubbling fluid-bed reactor presently used in the EERC hydrogen production project. The conditions for calcining involve the lowest gas velocity that can maintain stable operation in a deep char bed, so that the required char residence time at calcining temperature can be achieved with minimum gas flow and energy input. Calcining takes place at temperatures up to 1475°F (800°C). This unit also evaluates the potential for activated carbon production by using a combination of steam and flue gas. During integrated operation, hot gas leaving the calciner is directed to the carbonizer.

#### **Area 500 - Gas Quench and Liquid Separation**

The quench and separation area can receive gas from either the carbonizer or the calciner. The objective in the design of this area is to produce separate tar and oil fractions that meet primary product requirements. In addition, the quench system should provide trouble-free operation without tendency to plug and, ideally, should produce no wastewater condensate. The approach for this study is to provide both direct-contact tar and oil scrubbers (V-501 and Q-501) and direct-contact water scrubbers (V-502 and V-503). Three of the units are venturi scrubbers with liquid introduced on a flooded disk above the throat of the venturi or through a nozzle perpendicular to gas flow at the opening in the throat. This design allows flexibility both for cooling and particulate removal and for controlling plugging caused by particulates in the tar recycle stream.

A sidestream sampling unit is used to gather a fraction of the gas to determine removal efficiency of the quench units. Bench-scale testing is also possible to evaluate other potential condensable removal methods, such as using Rectisol.

Gas liquor from the scrubbers is pumped to 55-gallon drums for transfer to other tanks.

#### **Area 600 - Waste Treatment and Phenol Recovery**

Operation with appreciable steam in the carbonizing gas or on high-moisture coal without drying will inevitably produce wastewater condensate that must be treated prior to discharge. The wastewater cleanup methods that are available at the EERC include solvent extraction and distillation to remove phenols and trace organics, granular activated carbon for polishing before discharging, and alternatively activated sludge treatment of the raw waste stream. These processes will not be integrated in the operation of the MGPDU. The extraction step will be used only for study of phenol recovery. A high-temperature flare is used to discharge all product and vent gases.

## Area 700 - Char Upgrading

Requirements in this area have not been finally established. Upgrading operations that may be performed include grinding, screening, gravity separation, and magnetic separation. Char products to be evaluated include form coke, carbon pellets, char-iron ore pellets, and activated carbon. These operations will be subcontracted.

## Area 800 - Liquid Upgrading

On-site liquid upgrading at the EERC will be limited to distilling and hydrotreating the condensables utilizing existing equipment. Small lots of 5 to 10 gallons of oil and light oil will be stabilized by removing olefins and other gum-forming compounds. The stabilized liquid(s) will then be sent to a subcontractor for evaluation as a blending stock for No. 3 diesel fuel. Evaluation of the oil, light oil, and crude phenol streams for production of chemicals (e.g., phenol and benzene) will be performed by subcontractors off-site. No pretreatment or stabilization is planned for the liquids in this instance. These products will be upgraded only in the quantities needed for end-user testing.

## NOMENCLATURE

### MGPDU Unit Names

#### Letter Codes

- T - Storage Tank or Hopper
- C - Cyclone, Knockouts, etc.
- H - Heat Exchanger (heating or cooling)
- R - Reactor
- A - Sieve Column
- B - Fired Apparatus - Boiler, Flue Gas Generator
- P - Pumps
- Q - Quench Towers
- D - Distillation
- E - Liquid/Liquid Extraction
- F - Feeders
- S - Venturi Scrubbers
- V - Valve
- W - Activated Sludge

#### Area Codes

- 100 - Coal
- 200 - Utilities
- 300 - Carbonization
- 400 - Calcining/Drying
- 500 - Gas Quench and Liquid Separation
- 600 - Waste Treatment and Phenol Recovery
- 700 - Char Upgrading
- 800 - Liquid Upgrading

## EERC/AMAX MGPDU Equipment List

<u>ID No.</u>	<u>Name</u>
B-201	Steam Boiler
B-202	Steam Superheater
A-201	Boiler Feedwater Treatment
T-201	Sparge Tank
H-201	Dowtherm System
R-301	Carbonizer
T-301	Carbonizer Feed Hopper
F-301	Carbonizer Feeder
B-301	Carbonizer Flue Gas Generator
C-301	Primary Carbonizer Cyclone
T-302	HV Char Storage Bin
C-302	Secondary Carbonizer Cyclone
T-303	Char Fines Collection Bin #1
R-401	Calciner
T-401	Calciner Feed Hopper
F-401	Calciner Feeder
B-401	Calciner Flue Gas Generator
C-401	Calciner Cyclone
T-402	LV Char Storage Bin
C-402	Secondary Carbonizer Cyclone
T-403	Char Fines Collection Bin #2
S-501	Tar Venturi Scrubbers
H-501	Tar Cooler
P-501	Tar Quench Circulation Pump
H-505	Venturi Scrubber Cyclone Heater #1
S-502	Water Venturi Scrubber
H-502	Tar/Oil Cooler
P-502	Oil/Water Circulation Pump #1
H-506	Venturi Scrubber Cyclone Heater #2
Q-501	Oil Sieve Tower
H-503	Oil Cooler
P-503	Oil Quench Circulation Pump
S-503	Venturi Scrubber
H-504	Oil/Water Cooler
P-504	Oil/Water Circulation Pump #2
H-507	Tar Transfer Barrel Heater
H-508	Tar/Oil Transfer Barrel Heater
T-501	Tar Transfer Tank
T-502	Tar/Oil Transfer Tank
T-503	Oil/Water Transfer Tank #1
T-504	Oil/Water Transfer Tank #2
T-505	Tar Sample Vessel
T-506	Tar/Oil Sample Vessel
T-507	Oil/Water Sample Vessel
P-505	Condensate Transfer Pump

(continued)

<u>ID No.</u>	<u>Name</u>
Q-601	Emergency Tar Quench Vessel
B-601	Flare
C-601	Flare Knockout Pot
T-601	Wastewater Storage Tank
P-601	Wastewater Pump
E-601	Extraction Column
T-603	Spent Solvent Storage Tank
H-602	Solvent Condenser
D-601	Solvent Recovery Column
H-601	Solvent Recovery Reboiler
T-606	Crude Phenol Storage Tank
T-604	Clean Solvent Receiver Tank
T-605	Clean Solvent Feed Tank
P-602	Solvent Pump
T-602	Solvent Ext. WW Storage Tank
A-601/3	WW Polishing Adsorber #1, #2, #3
W-601	Activated Sludge Unit

**APPENDIX B:**

**UND ENERGY AND ENVIRONMENTAL RESEARCH CENTER  
4-LB/HR CONTINUOUS FLUIDIZED-BED REACTOR (CFBR)  
MILD GASIFICATION UNIT DESCRIPTION**



## COAL FEED SYSTEM DESIGN

Figure B1 shows the coal feed system in relation to the bottom of the reactor. A "star" feeder, which is not shown, was placed directly above the 2-inch flange shown in the figure. This feeder drops a specific volume of coal at selected intervals into the auger system. A small amount of purge gas is also fed into the auger system. The purge and high-speed auger are used to swiftly move the coal into the reactor before devolatilization can occur. Thus, the coal will be out of the feed system before agglomeration can occur to plug the feed system.

Plugging often occurs in small coal feed systems because a small volume of material moves through a very narrow opening, coal particles stick due to high-moisture content, and backflashing of hot gases from the gasifier causes swelling. Plugging had been experienced on the 30-lb/hr pressurized fluid-bed gasifier (PFBG) used on the Hydrogen Production from Coal Project. The problem was resolved on the PFBG by slightly pressurizing the coal hopper and purging the auger; consequently, these features were added to the design of the 4-lb/hr CFBR. The coal feed system has been calibrated for mass flow rates for several of the feed coals. Since the densities of the coals are slightly different, the star feeder revolution rate will vary with coal rank and crush size in order to maintain a constant mass flow rate. The mass flow rates for the feed system lie between 0.5 lb/hr and 8.0 lb/hr.

## REACTOR

The reactor was constructed of 316H stainless steel, Schedule 80 pipe. Figure B2 shows an isometric drawing of the unit. Figure B3 shows the machine drawing of the reactor, which includes thermocouple numbers and heights. The first section, which is attached to the coal feed system, is made of 3-inch pipe and is 33 inches in length. The next section is made of 4-inch pipe, 18.75 inches in length. The two sections are connected with a 316H-weld reducer. The top and bottom flanges (1500 lb) are composed of 316H-grade stainless steel, with Flexicarb stainless steel gaskets rated to 1650°F (900°C) and 200 psia. The unit was designed such that the top of the fluid bed lies 33 inches above the coal injection point. A char off-take leg at the top of the bed is the primary means of solids removal from the reactor. A ball valve facilitates the collection of char product while the system is operating.

The gasifier currently uses two ceramic fiber heaters capable of achieving temperatures of 1800°F (980°C). The bottom heater is rated at 2500 watts and the top at 1775 watts. These heaters will maintain the gasifier temperature and eliminate hot spots. Using external heaters allows the evaluation of internal and external heating methods for process development and scaleup.

## CYCLONE

A 3-inch-diameter cyclone is the secondary means of solids removal from the system. Like the char collection pot on the reactor, a ball valve allows the changing of the solids catch pot while the system is operating. The

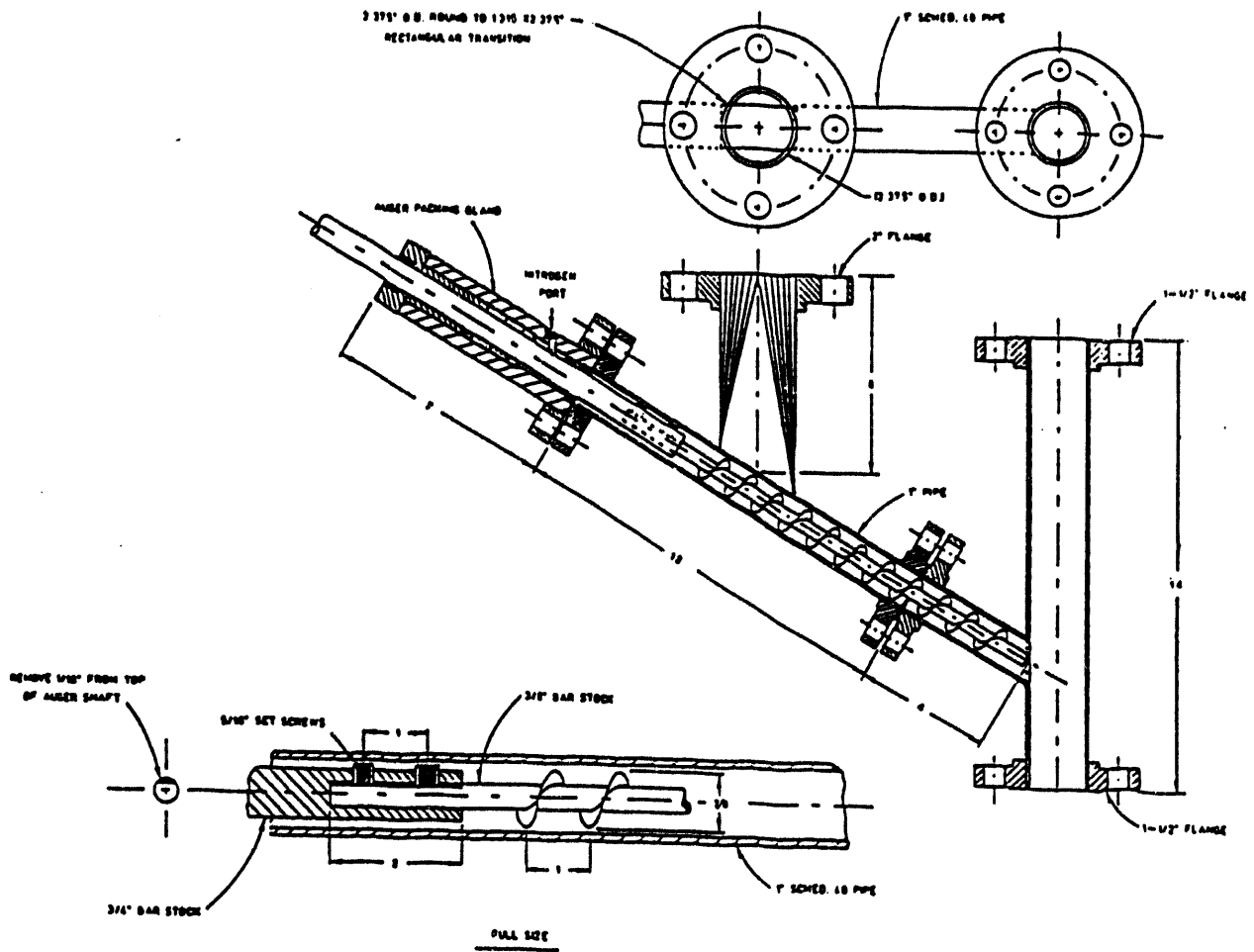


Figure B1. Coal feed system for the CFBR.

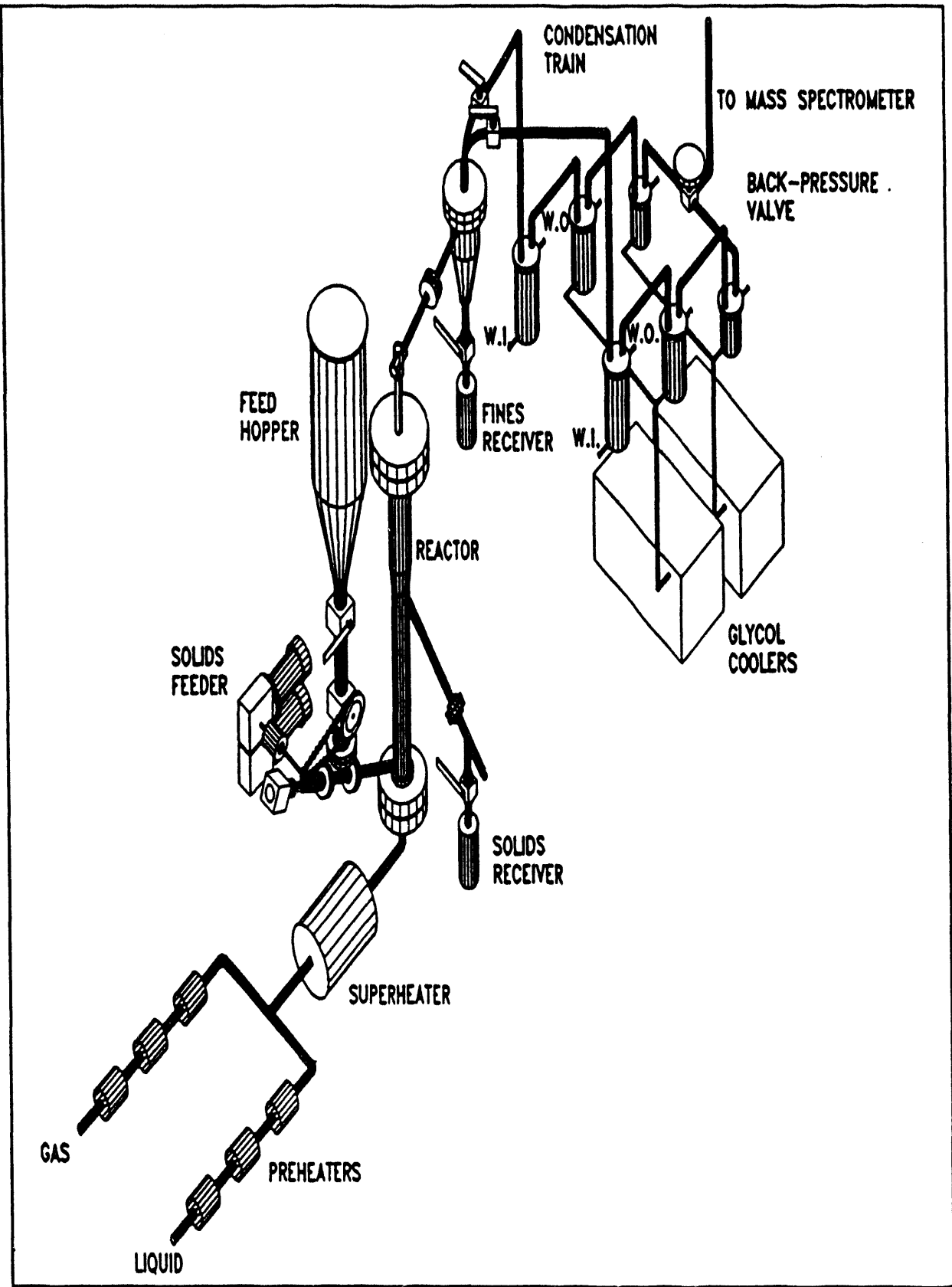


Figure B2. Four-lb/hr CFBR schematic.

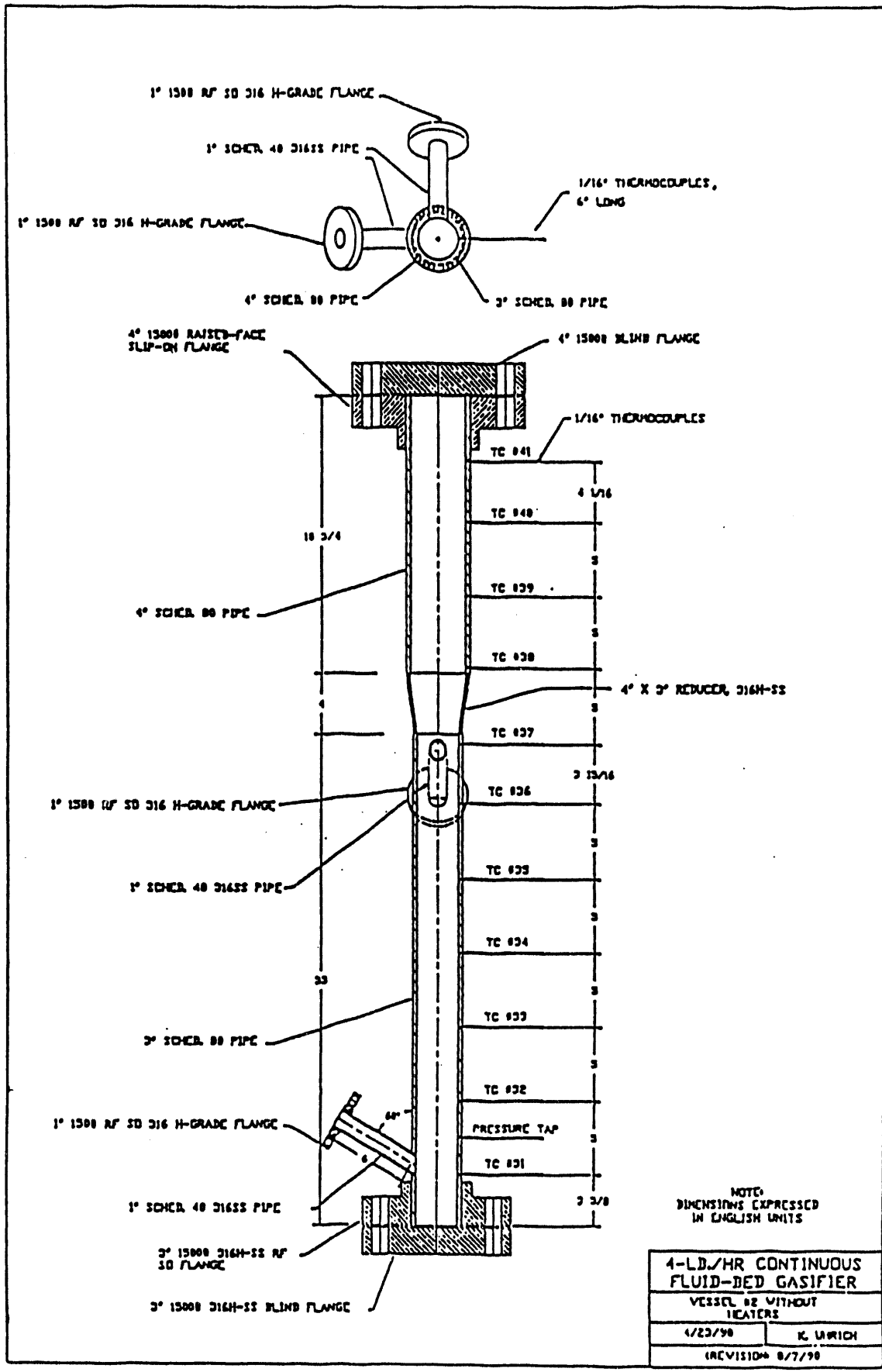


Figure B3. Four-lb/hr continuous fluid-bed gasifier.

cyclone is made of Schedule 80, 3-inch, 316H stainless steel pipe. It is heated with a ceramic fiber heater capable of operating at a temperature of 1650°F (900°C) and 200 psia. During preliminary tests, large quantities of char carryover in the condensate stream from the cyclone were not observed; therefore, a secondary filter was not needed for this system.

### **CONDENSER SYSTEM**

Three 4-inch-diameter vessels are used to remove all condensables from the gas stream. Two separate trains were installed: one for mass balance sampling, and the other for heatup, un-steady-state conditions, and cooldown. The first condenser pot is indirectly cooled by water and typically cools the gas stream from 570°F (300°C) to 200°F (95°C). The next two condensers are glycol-cooled. The exit gas temperature is typically 50°F (10°C). A glass wool filter was used to capture aerosols passed through the condenser system.

### **INSTRUMENTATION AND CONTROL**

An integrated controller, PC-based software, and data acquisition system were developed for the unit. The unit has 16 Barber-Colman Series 990 temperature controllers, which are directly linked to an AT-compatible computer using Genesis® software. Data from this system are directly transferred to Lotus® spreadsheet work files, so that data reduction time is greatly reduced.