WRI-09-R003

PRODUCTION OF SUBSTITUTE NATURAL GAS FROM COAL

TOPICAL REPORT

Start Date July 2003
End Date June 2005

January 2009

By
Andrew Lucero

Work Performed Under Cooperative Agreement
DE-FC26-98FT40323 Task 39

For
Taylor Energy, LLC
Irvine, California

And
U.S. Department of Energy
National Energy Technology Laboratory
Morgantown, West Virginia

By
Western Research Institute
Laramie, Wyoming

Kamalendu Das
Task 39

DISCLAIMER

ABSTRACT

The goal of this research program was to develop and demonstrate a novel gasification technology to produce substitute natural gas (SNG) from coal. The technology relies on a continuous sequential processing method that differs substantially from the historic methanation or hydro-gasification processing technologies. The thermo-chemistry relies on all the same reactions, but the processing sequences are different. The proposed concept is appropriate for western sub-bituminous coals, which tend to be composed of about half fixed carbon and about half volatile matter (dry ash-free basis.) In the most general terms the process requires four steps 1) separating the fixed carbon from the volatile matter (pyrolysis) 2) converting the volatile fraction into syngas (reforming) 3) reacting the syngas with heated carbon to make methane-rich fuel gas (methanation and hydro-gasification) and 4) generating process heat by combusting residual char (combustion). A key feature of this technology is that no oxygen plant is needed for char combustion

TABLE OF CONTENTS

LIST OF TABLE AND FIGURES

<u>Table</u> **<u>Page</u>**

<u>Figures</u> **Page**

EXECUTIVE SUMMARY

The United States is facing a shortage of natural gas. In the past 10 years the price of natural gas has nearly tripled. The high prices, currently about $6.50/MMBtu, have already affected U.S. fertilizer, chemical, and steel making industries. As of mid 2003 eleven ammonia plants representing over 20% of the U.S. capacity for ammonia production, had shut down and only half the remaining capacity was operating.[1] Recently, the U.S. chemical industry estimated that more than $50 billion in business was lost to overseas operations due to the high natural gas prices.[2] Current proposed solutions are to increase drilling, pipe natural gas supplies from Alaska, and invest billions to enter the global liquefied natural gas (LNG) market. A fourth possible solution is to increase production of natural gas from the vast reserves of U.S. coal.

In 2003, Western Research Institute (WRI) and Taylor Energy, LLC began a project to develop a process to make low-cost pipeline-quality substitute natural gas (SNG) from coal. If successful, this could provide a secure domestic resource that would also serve to stabilize the cost of existing sources of well-derived natural gas. Taylor Energy, LLC, had developed a concept to convert coal to SNG using well-established counter-current cyclonic processing methods in a novel sequence. A three-year bench-scale and pilot-scale project was proposed to prove the concept and prepare it for commercialization. The goals of the first year of the project were to design, construct, and test large bench-scale system to generate sufficient data to design, fund, and construct a pilot-scale unit. The second year of the project was planned to be focused on design, construction, and testing of a pilot-scale version of the technology. Plans for the third year of the project included designing a commercial demonstration project including detailed engineering, cost estimates, and environmental and economic performance projections.

During the first year of the project, a large bench-scale system (mini-pilot) was designed to convert approximately 30 lbs/hr of coal to SNG. Equipment was procured and assembly of the plant was nearly completed when Taylor Energy could not continue its cost share obligations to the project. Work on the project was stopped in fall 2004. Since it appears certain that Taylor Energy will not be able to complete its obligations in the future, this report has been prepared to document progress to date and close the project.

INTRODUCTION

The objective of this project is to develop a process to produce substitute natural gas (SNG) from coal. This approach provides an ideal long-term source of domestic energy because it (SNG) is ultra-clean burning, ideal for future technology uses, and because a vast pipeline distribution system already exists within the United States. Since it is derived from the United States' most abundant natural resource, coal, it offers a long-term source of abundant energy. In addition it offers potential solutions to environmental issues associated with burning coal, and will likely offer a route to utilize coal when the "hydrogen economy" begins to materialize.

The concept provides 3 key advantages over direct burning of coal for power. First, mercury emitted from coal fired power plants (about 48 tons per year) falls back to earth and finds its way into streams and lakes where bacteria convert it to methyl-mercury, which is absorbed by plants, then consumed by insects and fish. It is reported that, "fish can have methyl-mercury concentrations several million times higher than the surrounding water." (P. Silva, Natural Resources Council) Wyoming coal has about a third less mercury compared to coal from other areas; however, the problem is that the mercury in Power River Basin (PRB) coal is elemental, which is difficult and expensive to remove. "Estimates released by the EPA predict that production of PRB coal will drop about 100 million tons (per year) once the mercury removal regulations take effect." (B. Boettecher, Laramie River Station Plant). The new regulations will go into full effect in 2007. Coal gasification methods, and particularly the production of SNG, are long-term solutions, which will enable the use of coal resources in environmentally friendly clean-fuel applications because elemental mercury would be easily removed from the SNG product before the gaseous fuel is delivered to market via pipeline.

Second, natural gas offers a hydrogen carrier for which a vast distribution network already exists. Recent news concerning the eventual conversion to the "hydrogen economy" has highlighted the lack of infrastructure for hydrogen distribution and general use. There are some who would respectfully submit that methane is the most appropriate "hydrogen carrier" for the present and well into the future. One version of this scenario is based on the fact that Hybrid solid oxide fuel cell (SOFC) technology being demonstrated today (by Siemens Westinghouse at 220 kW scale) has proven 60% conversion efficiency using natural gas as the fuel. With high methane conversion efficiencies and a vast fuel distribution system in place, the benefits of producing and transporting hydrogen may be difficult to justify, considering that H_2 is difficult to compress, difficult to handle because it leaks easily through valves, fittings, and closures, and causes the infamous hydrogen embrittlement; and ignition, flammability, and flame propagation rate are all troublesome. Compared to hydrogen, methane is much easier and safer to handle and utilize.

Third, fuel transportation costs in most electric power generation markets that use Power River Basin (PRB) coal contribute ½ to $^2/_3$ of the total cost for coal at the point of use. Aside from the clean-fuel benefits, SNG technology might provide a more economical means of delivering coal energy to the power generation markets when compared to the coal-train delivery system in use today. Cost effective SNG technology would enable the conversion of coal into a clean-fuel product for power generation at costs similar to or slightly higher than rail delivered coal for locations where pipeline capacity exists. Moreover, the gaseous fuel is compatible with emerging (within two decades) power generation technologies that rely on solid-state conversion methods (SOFC). In the near term, NG pipeline capacity is the limiting factor.

BACKGROUND

The first step of the process to produce natural gas from coal is obviously gasification. While the approaches and equipment used to convert coal to synthesis gas vary widely, they all rely on the same thermo-chemical reactions[3]:

Solid-gas reactions	Reaction heat kj/kg•mol	Process
(1) $C + O_2 \rightarrow CO_2$	393,790	Combustion
(2) $C + 2H_2 \rightarrow CH_4$	74,900	Hydro-gasification
(3) $C + H_2O \rightarrow CO + H_2$	-175,440	Steam-carbon
(4) $C + CO_2 \rightarrow 2CO$	-172,580	Boudouard
Gas-phase reactions		
(5) $CO + 2H_2O \rightarrow CO_2 + H_2$	2,853	Water-gas shift
(6) $CO + 3H_2 \rightarrow CH_4 + H_2O$	250,340	Methanation

In addition pyrolysis and hydro-pyrolysis reactions can produce carbon and methane in varying amounts.

There are several gasification technologies that have been used in commercial applications’. These include: Texaco Entrained Flow Gasifier, Shell Entrained Flow Gasifier, Lurgi Dry Ash Gasifier, British Gas/Lurgi Fixed-Bed Gasifier, E-GAS Entrained Flow Gasifier, and KRW Fluidized-Bed Gasifier.

The Texaco gasifier is a single stage entrained-flow (downward flow) slagging gasifier that reacts to coal slurry with oxygen. The Shell gasifier is a dry-feed entrained-flow (upward flow) pressurized slagging gasifier. The Lurgi Dry Ash Gasifer is a pressurized dry-ash moving bed (downward flow) gasifier. Steam and oxygen flow counter-current to a moving coal bed. The British Gas/Lurgi gasifier is a pressurized dry-feed fixed-bed slagging gasifier. The E-GAS (formerly Destec) gasifier is a slurry-feed, pressurized, up-flow, entrained slagging gasifier that operates in dual stages. Approximately ¾ of the feed is reacted with oxygen in the bottom stage and the remaining feed reacts with raw synthesis gas in the top stage. The KRW gasifier is a fluidized bed in which coal particles are reacted with oxygen. Both coal and oxygen are then reacted with steam at high temperature. All of these gasifiers require oxygen to produce a synthesis gas suitable for conversion to fuels. The gasifiers differ in the feed characteristics, flow paths, reagent contacting, slagging characteristics, and operating temperatures.

None of these gasifiers are specifically designed for methane production; however, they can be modified for that purpose. The basic avenues available are production of synthesis gas followed by methanation (Equation 6), or direct hydro-gasification of carbonaceous feedstocks (Equation 2).

A number of processes have been developed for production of Substitute Natural Gas (SNG) from carbonaceous feeds. Prior to 1980, processes specifically designed for the production of SNG were developed to pilot scale and, in some cases, developed to very large demonstration scale. However, only a few commercial SNG technologies are operational anywhere in the world today. In fact, except for the Great Plains Gasification Project, activities related to SNG production during the past 25 years have been minimal.

The Great Plains Project uses 14 proven Lurgi coal gasification reactors, converting coal into synthesis gas via partial oxidation, followed by methanation reactors. The capital requirements for this approach are quite high, and the process uses a huge air-separation process to produce pure oxygen required for the gasifier. There are other specific limitations related to the Lurgi reactor, including high oxygen consumption and the inability to use coal-fines (less than 6 mm), which could limit profitability somewhat. However, the Great Plains Project proves that SNG is technically feasible at large capacity. Long-term pipeline gas production from coal has averaged more than 137 M SCF per day, with current capacity at approximately 170M SCFD of SNG. The plant's many byproducts including ammonia, ammonium sulfate, phenol, cresylic acid, all serve to increase profitability. In addition, the plant sells 95 M SCFD of CO_2, which is used in enhanced oil recovery. This also illustrates the potential for producing SNG while sequestering CO_2.

In addition to the Lurgi gasification-methanation process, other historic SNG technologies developed more than 25 years ago include: HYGAS, BI-GAS, SYTHANE, HYDRANE, and AGGLOMERATED ASH PROCESSES[4]. The HYGAS process was developed by the Institute of Gas Technology, and was based on the hydrogenation of a fluidized bed of specially prepared coal. The process actually utilized 3 fluidized beds; the coal entered the top bed as a, slurry while the hydrogen entered the bottom bed and fluidized all three beds. The system operated at elevated pressure, 75-90 atm, which is conducive to the formation of methane. Synthesis gas from the gasifier was purified then converted to SNG in a methanation reactor.

The BI-GAS process was, developed by Bituminous Coal Research Inc. The system consisted of dual stages of gasification operating at approximately 930°C and 1670°C. Coal was introduced to the process in a, water slurry where it was initially separated and dried by raw product gas from the process. The dried coal powder entered the low temperature section of the gasifier with steam where it was de-volatilized and partially gasified. Char formed in the process was carried into a cyclone from which it was discharged into the high temperature gasifier. There it was reacted with steam and oxygen. The high temperatures turned the ash to slag, which was allowed to drop into a pool of quench water. The system was capable of processing a wide variety of coals, but the raw product gas normally required two successive methanation steps to be compatible with US natural gases.

The SYNTHANE process was, developed by the U.S. Bureau of Mines. The process was designed to operate with a wide variety of coals; however, coking coals were pretreated before injection to avoid problems with the fluidized bed. This was accomplished in a manner similar to the BI-GAS process by injecting the coal in, a, water slurry, drying it by contact with the gasifier overhead gas, and separating the dry coal and raw gas with a cyclone. The dried coal then entered the gasifier through a standpipe where it reacted with steam and oxygen at about 980°C in the fluidized bed. Raw gas was then sent to purification and methanation sections of the plant.

The HYDRANE process, also developed by the Bureau of Mines, was another process in which hydrogen was reacted with coal at elevated temperatures and pressures. The resulting char was gasified with steam and oxygen in a fluid bed to produce the hydrogen. The system was designed to process all types of coal without pretreatment.

The AGGLOMERATED ASH PROCESS was, developed by Union Carbide and the Battelle Research Institute. It is also based on a high-temperature fluidized bed, but avoids the use of oxygen by utilizing a separate char burner in which char and ash are oxidized by compressed air. Char is withdrawn from the surface of a high-temperature gasifier while agglomerated ash is drained from the bottom of the gasifier. The mixture of char and ash is sent to a burner where it is combusted with air. Hot agglomerated ash is then sent from the burner fluid bed back to the gasifier. Since the process operates at very high temperatures, 980-1100°C, very little methane is formed, and methanation duty is fairly high as a result.

These methods have all fallen from favor in recent years, except for an integrated hydro-gasification approach known as the ARCH process, which is currently being developed by the Japanese Coal Association. The process is intended for co-production of SNG and BTX (benzene, toluene, xylene.)

PROJECT OBJECTIVES

The overall goal for the project was to develop a process for conversion of coal into SNG using well-established counter-current cyclonic processing methods in a novel sequence that serves to react, activated carbon char with synthesis gas, both of which are derived from the coal feedstock in a highly integrated process. Specific objectives for the project were:

- The objective of the first year of the project was to conduct bench-scale proof-of-concept and scaling-feasibility testing. The goal of this portion of the work was to generate sufficient data to design, build, and test a pilot-scale unit.
    - Design and fabricate bench-scale experimental system.
    - Demonstrate ability to control flows of gases and solids (cold flow testing).
    - Conduct bench-scale tests demonstrating uniform, controllable, and stable operation with coal.
- The objective of the second year of the project will be to design, fabricate, and operate a pilot-scale facility to generate operational data sufficient to design and evaluate a commercial-scale facility.
- The objective of the third year of the project is to design a commercial demonstration project including detailed engineering, cost (+/-10%), and environmental and economic performance projections.

PROPOSED TECHNOLOGY

The purpose of this project was to demonstrate a novel gasifier concept designed to facilitate the production of SNG from coal. The proposed concept is appropriate for western sub-bituminous coals, which tend to be composed of about half fixed carbon and about half volatile matter (dry ash-free basis.)

Table 1. Characteristics of Western Sub-bituminous Coal, Wyoming

Proximate (as received)	(wt %)
Moisture	28.0
Ash	5.1
Fixed Carbon	33.8
Volatile Matter	33.1

In the most general terms the proposed process requires four steps 1) separating the fixed carbon from the volatile matter (pyrolysis or de-volatilization) 2) converting the volatile fraction into syngas (reforming) 3) reacting the syngas with heated carbon to make methane-rich fuel gas (methanation and hydro-gasification) and 4) generating process heat by combusting residual char (combustion). A key feature of this technology is that no oxygen plant is needed for char combustion. In addition, highly efficient counter-current heat-recovery methods are used to direct heat from the char combustion section to the endothermic gasification and reforming stages of the process. The gasifier is designed to aggressively mill the coal particles while thermo-chemical reactions are taking place. The purpose of the milling is to increase the surface area of reactive particles, both mineral and carbonaceous and therefore increase thermo-chemical reaction rates. In addition, metals, metal oxides, and alkali present in the coal may serve to catalyze reactions of interest[5,6]. It is anticipated that the milling action combined with the planned large recycle rates of solids and fuel gases will serve to liberate minerals that can catalyze hydro-gasification and methanation.

In its simplest form the gasifier is vaguely similar to the Agglomerated Ash Process or Battelle's dual fluidized bed biomass gasifier[7]. In the proposed process, instead of fluidized beds, a jet spouted bed and a cyclone would be utilized. In addition, the functions of each reactor are split into multiple reactors. Since oxidizing and reducing functions are in separate reactors, the system can produce SNG undiluted with nitrogen in air-blown configuration; however, to produce a sequestration ready off-gas stream, the gasifier can be oxygen-blown.

Again because of the separate oxidizing and reducing reactors, oxygen can be supplied as a CO_2/O_2 mixture from a process such as BOC's Cyclic Auto-thermal Recovery (CAR) process. BOC's CAR process utilizes the oxygen storage capacity of perovskite materials at high temperatures and involves cyclic operation with traditional fixed-bed vessels containing the material in granular form[8]. The process consists of two main steps: 1) oxygen sorption and 2) oxygen release. During Step 1, air is passed through one bed to allow sorption and storage of oxygen; while in Step 2, a sweep gas (flue gas or steam) is passed through the other bed to release stored oxygen. The process requires dual beds to operate in a continuous fashion.

Figure 1 shows a simplified flow diagram of the process. In the jet spouted bed reactor, de-volatilization of the coal occurs in addition to the steam carbon reaction and hydro-gasification. Fuel-gas and un-reacted char are transferred to Cyclone 1, where the char is milled before it drops through an airlock valve to Cyclone 2. Combustion of the char occurs in Cyclone 2 concurrent with additional milling of solids. The hot solid ash drops through another airlock valve into the fuel-gas recycle stream where it begins reforming fuel-gas as it transfers heat back to the jet-spouted bed reactor. The purpose of the airlock valves is to allow transfer of solids without contaminating fuel gas with nitrogen (if air-blown) or excess CO_2 (if oxygen blown from CAR Process). In either case, separating the oxidizing and reducing reactions in this fashion allows this gasifier system to avoid the capital and operating costs associated with a large oxygen separation system. Capital and operating costs of the CAR process are projected to be about 60% of those for a cryogenic oxygen plant. Figure 2 shows how the gasifier could be integrated with BOC's CAR process.

Figure 3 shows a diagram of the planned bench-scale (mini-pilot) plant at WRI. For simplicity, valves and instrumentation have been omitted. Two additional cyclones are included because residence time may be insufficient for combustion in one cyclone. The additional cyclones allow some of the functions of each portion of the plant (oxidizing or reducing reactions) to be split into additional reactors. Cyclone 4 allows for final removal of solids from the system. A venturi scrubber helps recapture and recycle fine particulates. WRI planned to operate the system at atmospheric pressure; however, it may be possible in the future to operate at elevated pressures providing that suitable airlock valves can be obtained.

Another advantage of this approach is that the specific hardware needed to carry out the proposed processing sequence is based on the use of well-known cyclonic processing techniques that are proven at very large scale for industrial cement calcining. Up to five stages of integrated counter-current gas-solids contacting are employed commercially for high-temperature cyclonic roasting of limestone. The proposed coal processing method is highly integrated and several thermo-chemical processes are occurring simultaneously. The hardware configuration is designed to accomplish of three synergistic cycles:

- Reducing gases follow one pathway, with a high degree of recycle.
- Oxidizing gases follow a separate pathway, and exhaust through a boiler.
- Solids transfer heat as they circulate between the oxidation and the reduction cycles.

The key challenge is then to move solids from the oxidizing reactor to the reducing reactors to transfer heat from exothermic reactions to endothermic reactions. Transferring the heat without contaminating fuel gases with nitrogen (or excess CO_2) will make the process highly efficient. The proposed approach to make the solids transfer will be to utilize “Double-Dump” airlock valves used commercially in the cement industry. A second major issue will be the fate of tars formed during the pyrolysis reactions. Managing this issue will required careful balancing of the solids recycle rate compared to the coal feed rate. A third serious issue will be to determine the fate of contaminants present in the coal. The system is conceived so that contaminants of concern such as mercury and sulfur will be carried into the synthesis gas/SNG product stream for treatment. WRI had planned to determine what (if any) fraction of the contaminants leaves the system in the off-gas stream.

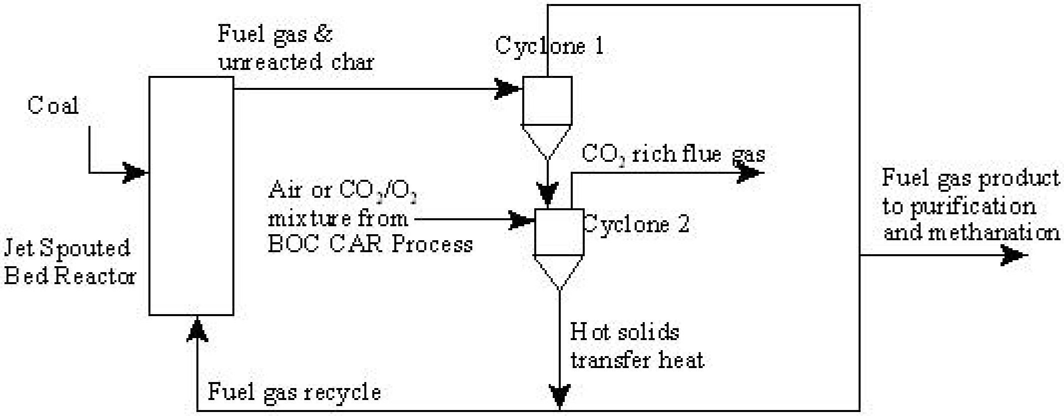

Figure 1. Simplified Flow Diagram of WRI Gasifier

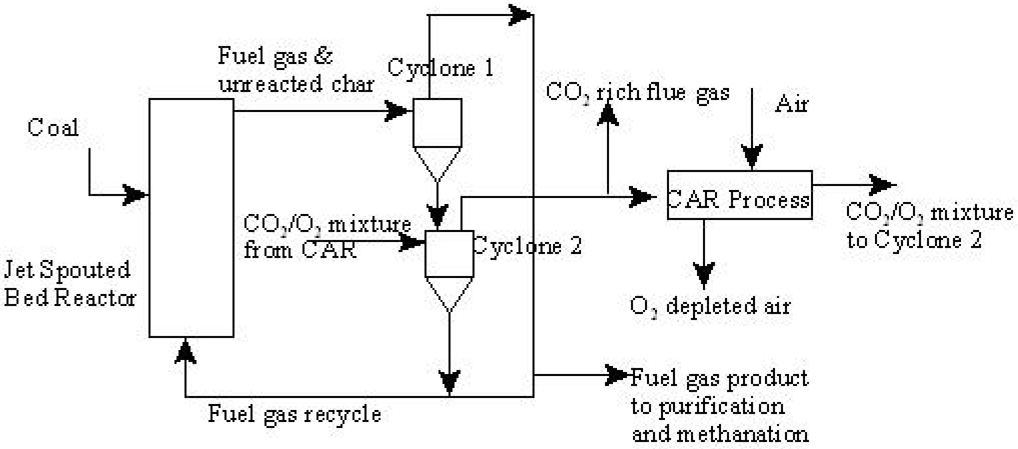

Figure 2. WRI Gasifier Integrated with BOC CAR Process

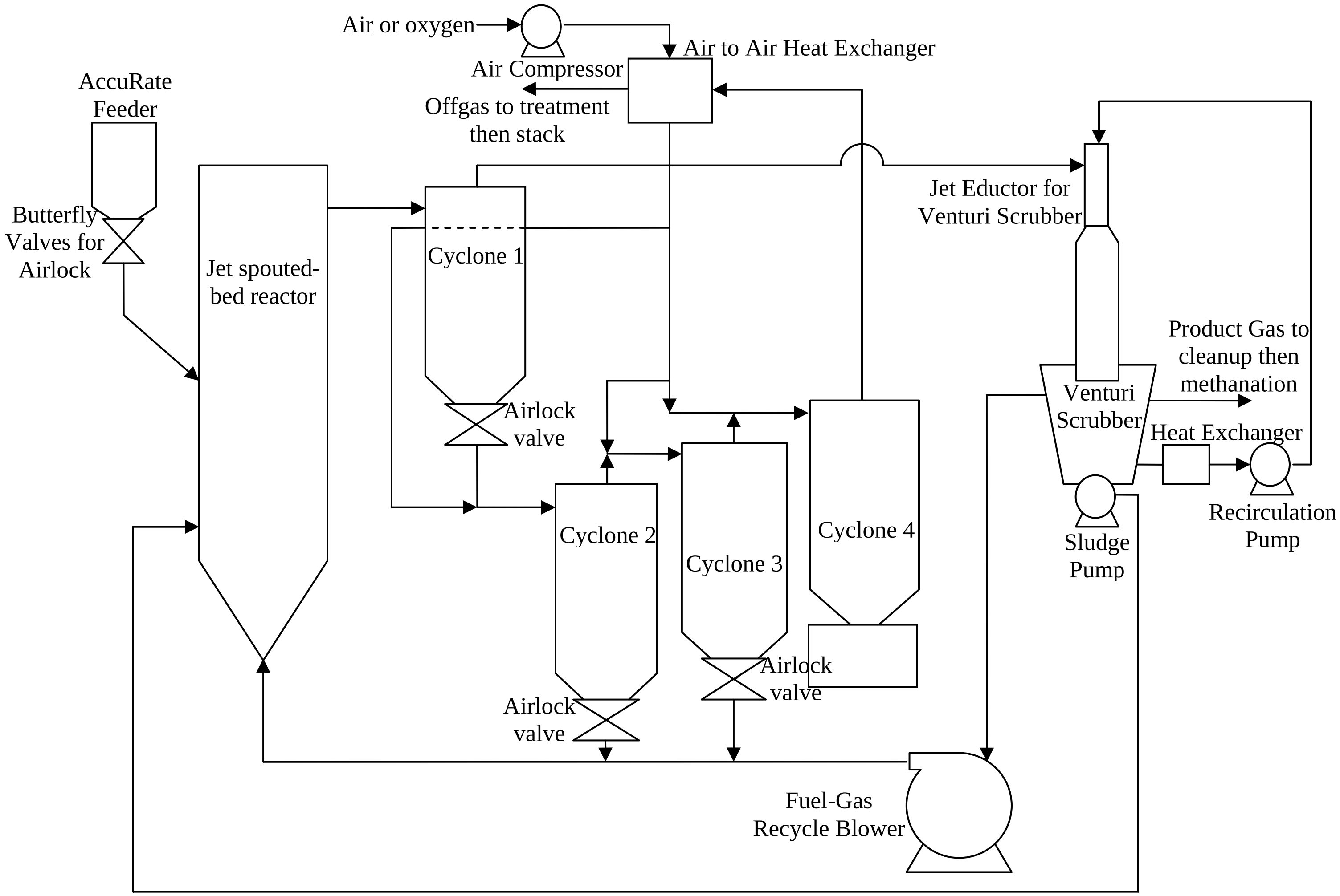

Figure 3. Simplified Flow diagram for WRI Mini Pilot-Scale Gasifier

STATUS

During the project, a large bench-scale (mini-pilot) plant was designed to convert sub-bituminous coal to SNG. Valves, pumps, blowers, and other commercially available components of the system were purchased. Cyclones were designed and fabricated using cast refractory inside stainless shells (See Figure 4). Several cold flow experiments were conducted using various models to generate information needed to design the jet-spouted bed reactor (Figures 5 and 6). A venture scrubber was designed and fabricated, and most of the interconnecting piping was completed, and ancillary pumps, blowers, and valves installed (See Figure 7).

To complete the system, a number of tasks still remain. First, fabrication of a jet-spouted-bed reactor must be completed. Pressure, flow, and temperature instrumentation still need to be added to the system. Electrical wiring will require completion prior to connecting the instrumentation to a data acquisition and control system. Finally, the system needs to be installed at WRI's Advanced Technology Center.

To demonstrate feasibility of the concept at a minimum the following two tasks must be completed.

1. Demonstrate ability to control flows of gases and solids (cold flow testing). Initial tests of the system should be conduced at ambient temperature to demonstrate capability to manage flows of solids and gases through the system. Portions of the piping may be temporarily replaced with transparent materials to aid in troubleshooting. Initial plans should include testing the system with different inert gases in each section of the system (perhaps argon in the reducing reactors and nitrogen in oxidizing reactors) to obtain an indication of cross contamination during operation.

2. Conduct experiments demonstrating uniform, controllable, and stable operation with coal with the system in air-blown configuration. "Hot" tests should be conducted with the system in air-blown configuration. The purpose of these tests is to demonstrate the capability to produce fuel gas without contamination with nitrogen. Specifically, the first objective is to gasify the coal while demonstrating "clean" separation of oxidizing and reducing reactions. The system should be operated for periods of time sufficient to demonstrate steady-state production of fuel-gas with SNG. For the bench-scale (mini pilot) plant, production of fuel gas containing 20 to 25% (by volume) of methane would be considered a strong success.

At this point the project has been stopped due to funding issues. The concept appears to be strong, but no experimental data has been generated to support that conclusion. It is hoped that a new funding source can be identified sometime in the future.

Figure 4. Internal view of cyclone cast in refractory.

Figure 5. First Cold-Flow Model for Jet-Spouted Bed Reactor

Figure 6. Second Cold Flow Model For Jet Spouted Bed Reactor

Figure 7. Photograph of Partially Completed SNG Mini Pilot Plant

APPENDICES

Bibliography and References

[1] Mathers, K. “Fertilizer Industry Weighs in on Energy Crisis at Natural Gas Summit,” The Fertilizer Institute, June 26, 2003.

[2] VandenHeuvel, C., “Chemical Makers Applaud Senate for Passing Energy Legislation,” American Chemistry Council, Statement June 28, 2005.

[3] Perry, R. H., Green, D. W., Maloney, J. O., “Perry’s Chemical Engineers’ Handbook Sixth Edition,” McGraw-Hill, 1984.

[4] Lom, L.W., Williams, A.F., “Substitute Natural Gas Manufacture and Properties,” Halstead Press, Applied Science Publishers, 1976.

[5] Ohtsuka, Y., Asami, K., Yamada, T., Homma, T., “Large Rate Enhancement by Iron Catalysts in the Low-Temperature Hydrogasification of Brown Coal Under Pressure,” Energy & Fuels; 1992; 6(5); 678-679.

[6] Haga, T., Nishiyama, Y., “Promotion of Iron-Group Catalysts by a Calcium Salt in Hydrogasification of Coal Chars,” Ind. Eng. Chem. Res.; 1989; 28(6); 724-728.

[7] Paisley, M., A., Litt, R., D., and Creamer, K., S., “Gasification of Refuse Derived Fuel in a High Throughput Gasification System,” Energy from Biomass and Wastes XIV Conference, January 29-February 2, 1990, Lake Buena Vista, FL.

[8] Tamhankar, S., Acharya, D., Zeng, Y., Ramprasad, R., and Ramachandran, R., “A Novel Oxygen Supply Method for Oxy-Fuel Combustion,” Pittsburgh Coal Conference, Sept. 23-27, 2003, Pittsburgh, PA.

Boettecher, B. Casper Star Tribune. April 22, 2003. “Mercury Regs could Cut Into Coal Production.” Associated Press.

Silva, P. Casper Star Tribune. April 22, 2003. “Mercury Regs could Cut Into Coal Production.” Associated Press.