

SHELL MDS

The Shell Middle Distillate Synthesis (MDS) concept is a nearly commercial two-stage gasification-to-liquids process that permits variation of middle distillate (naphtha, kerosene, and gas oil) yields. It is based on modernized, classical Fischer-Tropsch technology using synthesis gas that can be produced from coal. The principal products are middle distillates but hydrocarbons ranging from low molecular weight paraffins to waxes are also produced. The gasifier is capable of using most coals as feedstock. A Shell MDS plant using methane rather than coal as the raw material is under construction in Malaysia.

3.2.3 Liquefaction Concepts

AGFLOTHERM

This concept involves the simultaneous beneficiation of coal and an upgrading of heavy oil or bitumen. Oil agglomeration of the coal followed by flotation separation step and then thermal treatment at moderate temperatures and atmospheric pressure produces a processed oil with reduced heteroatom content and density and a low-ash, low-moisture solid fuel. The processed oil could be further treated in a conventional petroleum refinery, and the solid fuel sold for utility/large scale industrial use. This concept, advanced by the Alberta Research Council (Canada), is at the bench-scale level of development.

CATALYTIC TWO-STAGE LIQUEFACTION

This coal liquefaction concept uses a two-stage process involving thermal dissolution of coal under the presence of a catalyst in the first stage, followed by catalytic hydrogenation of the coal extract. The concept design, advanced by Hydrocarbon Research, Inc., is similar to the Close-Coupled Integrated Two-Stage Liquefaction (CC-ITSL) technology used in the Wilsonville Advanced Coal Liquefaction Facility's 6 tons per day process development unit. The major products include transportation fuels, fuel oil, and utility turbine fuel. Research work is directed toward process improvements such as reduction in the severity of operating conditions, improved catalysts, and the use of cleaned coals.

COAL DEPOLYMERIZATION - LIQUEFACTION

This is a new method for breaking down and solubilizing coal into liquids using chemical techniques. In the initial process step, coal is depolymerized under mild reaction conditions and results in an improved product yield. Light liquid fuels are the objective. Process development at the Department of Fuels Engineering, University of Utah, is at the bench scale level. As with many conversion technologies, the product yields have been shown to be dependent on the type of coal used as feedstock.

COAL/OIL COPROCESSING

Coal/oil coprocessing is the simultaneous reaction of coal and poor-quality petroleum feedstocks in the presence of hydrogen, to produce clean distillable liquids and fuel gases. The liquids that are generated can be used directly as clean power plant fuels or upgraded to produce transportation fuels. One concept, as developed by Hydrocarbon Research, Inc., has been tested at the 3 tons per day process development unit level. A prototype plant using this technology was proposed for a Warren, OH site, and was selected for funding in the first round of the DOE Clean Coal Technology program. The project was eventually terminated in June 1991, prior to start of detailed design and construction.

ENHANCED COAL LIQUEFACTION BY RAPID HEATING

The rapid heating approach is being developed to liquefy coal with high conversion efficiency while reducing hydrogen consumption. Pulverized coal is catalytically converted under rapid heating conditions (heat rate of approximately 1,000° F per second) into liquids, while minimizing hydrocarbon gas formation. Bench scale development is being performed at the Department of Fuels Engineering, University of Utah. This process is at an early (bench-scale) stage of development. However, the high conversion efficiency has been confirmed experimentally.

LIQUID SOLVENT EXTRACTION

Solvent extraction is used for noncatalytic direct hydrogenation and liquefaction of coal, by contacting coal with a hydrogen-donor solvent. The process as proposed by the British Coal Corporation essentially involves two stages, with the first stage being low-pressure thermal liquefaction and high temperature filtration, with catalytic hydrocracking of the coal extract as the second. The goal is to economically produce, from any type of coal, naphtha, middle distillates fuels, and fuel gases (e.g., Liquefied Propane Gas). Process development is at the 2.5 ton per day pilot scale at Point of Ayr, North Wales.

NEDOL

This Japanese concept involves the combination of three processes similar to U.S. processes: direct hydrogenation, solvolysis, and solvent extraction. The arrangement consists of a thermal dissolution stage followed by a solvent hydrogenation stage. The major products include naphtha and middle distillates, for use as chemical feedstocks or as precursors to premium transportation fuels as well as fuel gases such as Liquefied Propane Gas. This concept being developed by the New Energy Development Organization (NEDO) of Japan is being studied at the 1 ton per day process development unit level using bituminous coal. A 150 ton per day demonstration plant is planned for 1994 operation.

NIPPON BROWN COAL LIQUEFACTION

This concept is based on the two-stage liquefaction of high-moisture Victorian (Australian) brown coal, and consists of four unit processes: dewatering, primary hydrogenation,

deashing, and secondary hydrogenation. The major products include liquid hydrocarbons (naphtha, middle distillates) which can be upgraded to produce premium transportation fuels such as gasoline and kerosene and industrial boiler fuels. This concept developed by the Nippon Brown Coal Liquefaction Co. Ltd., was demonstrated at a 50 ton per day pilot facility in Maxwell, Victoria. Operations were terminated in October 1990, and the unit is being dismantled.

3.2.4 Bioprocessing Concepts

BIOCONVERSION OF COAL TO ALCOHOL FUELS

This concept has two variations for the production of chemical feedstocks and alcohol fuels through bioprocessing. In the first, a direct method, pulverized coal is solubilized into a liquid by microorganisms. The resultant liquid is then gasified (some liquids could be drawn off and upgraded to higher-value products if there is sufficient quantity and quality). Another set of microorganisms is then used to produce the alcohol fuels. In the indirect method, coal is gasified using conventional gasification techniques. Microorganisms then convert the syngas to acetate (chemical feedstock) and ethanol (chemical feedstock, fuel). The concept is being studied at the bench scale at the University of Arkansas and is in the very early stages of formulation.

LIGNITE REFINERY

This lignite bioprocessing concept has been examined by Houston Lighting & Power Co. The proposed concept would produce benzene, toluene and xylene liquid fuels, organic acids for chemical feedstocks, carbon dioxide, and methane for utility boiler and combustion turbine applications. Methane-producing microbes are used to gasify a pre-treated lignite slurry in bioreactor caverns built for cost-saving reasons in underground rock caverns. With the plant operational assumptions and Texas lignite as the feedstock, the concept did not have the economic potential required by Houston Lighting & Power. This concept was evaluated as a conceptual design.

3.3 CONCLUSIONS AND RESEARCH NEEDS FOR REFINERY CONCEPTS

The individual concepts within a category have many common features that often lead to common products, markets, applications, and R&D objectives and requirements. The following comments address some of the issues common to the concepts within each refinery category. More general comments that encompass all refinery categories are also provided.

3.3.1 Devolatilization Coal Refineries

3.3.1.1 Conclusions

The ten coal refinery concepts described in the devolatilization category are designed to achieve the overall objective of reducing the retorting conditions typically

associated with the production of coal liquids. While this objective may be met, several additional issues arise with concepts in this refinery category. These additional issues include low liquid yield, potential extensive upgrading requirements for these liquids to meet specifications equivalent to those for currently used liquids, and the economic value of the solid (char) that remains after the devolatilization process. This latter issue arises from the lower volatility and higher ash, and similar sulfur content of the char as compared to the original coal feedstock. Issues such as process efficiency, materials handling, resource requirements, and overall economics also exist with these concepts as they do with many others. The devolatilization refinery concepts address these and other issues although the specific focus of any R&D activities that may be undertaken could vary from one concept to the next.

3.3.1.2 Research Needs

All of the concepts in the devolatilization category could benefit from R&D activities directed toward the scaleup of current operations to capacities appropriate to evaluate the concept at near commercial conditions and for demonstration of long-term, successful operation. Several of these concepts are currently at the bench or PDU scale so that significant scaleups would be needed to verify these parameters at near-commercial scale. Development of many of the mild gasification processes in this category is being supported by the DOE Surface Coal Gasification program.

It could be advantageous to the maturation of these concepts to evaluate the impacts of different coals on the design, operation, and economics of devolatilization refineries. Many of the concepts have been focused on Western subbituminous coals because of the desire to produce a low-sulfur char. Greater understanding of the influences of coal characteristics on the products and costs of devolatilization refineries would assist in the determination of the full potential of these coal refineries in the marketplace.

Changes in process requirements, products, and expected market conditions can significantly impact the economics of any developing concept. This realization may be particularly important with devolatilization technologies due to the mix of solid and liquid products that is produced. Not only will the costs of these products change as the concepts become more definitive, but the value of the products can also change significantly with time. This is particularly important to the extent that petroleum products can be displaced by products from a coal refinery. Because the cost of the petroleum products can change greatly due to geo-political forces, the value of displacement products can also change. Careful examination of the economic impacts of changing costs and changing value for products could help to reduce the uncertainties of economic competitiveness of concepts in the devolatilization category.

3.3.2 Gasification Coal Refineries

3.3.2.1 Conclusions

In general, the coal refinery concepts in the gasification category are probably the most advanced of those considered. The seven concepts presented include some that are operating commercially and others based on components that have been demonstrated on a commercial scale but have not been integrated into a complete system. The principal products from the gasification-based, coal refineries are liquids derived from synthesis gas, and chemicals which can be used directly or used as a feedstock in the making of other chemical products. Some of these concepts also produce electricity.

Further design and operational experience will be very beneficial in the maturation of these concepts. Those concepts consisting of components which have been used individually but which have not been incorporated in the manner proposed for these concepts will benefit the most from such additional experience. Further experience with these concepts, including the use of several coal types, will be invaluable in determining optimum design and operating conditions for these coal refinery concepts.

3.3.2.2 Research Needs

Specific items where additional R&D activities could prove beneficial include the development of catalysts that are more tolerant to sulfur and to trace elements in the coal, improvement of overall process efficiency, and the development of new catalysts for conversion of synthesis gas to chemicals and liquid fuels that are geared to lower hydrogen-to-carbon monoxide ratios in the synthesis gas. Catalyst development is being supported by the DOE Coal Liquefaction R&D program, while advanced gasification power systems are a major part of the DOE Surface Coal Gasification R&D program.

Several of the concepts examined in this category involve the production of methanol. Conventional methanol synthesis takes place in the gas phase with the reaction maintained at a relatively slow rate to prevent damage to the catalyst. A new technology called the Liquid Phase Methanol (LPMEOH) Process has been developed by Chem Systems, Inc. and Air Products and Chemicals, Inc., in which methanol synthesis proceeds in a liquid medium which acts as a heat sink. This method has the ability to directly process the carbon monoxide-rich gas produced by coal gasifiers and potentially has lower costs than the traditional vapor-phase processes. Development of this technology has been supported by the DOE Coal Liquefaction R&D program. The process has been successfully tested at up to pilot scale, and has no further R&D needs, other than a large-scale demonstration to attract commercial interest.

3.3.3 Liquefaction Coal Refineries

3.3.3.1 Conclusions

The eight concepts considered in the liquefaction category of coal refineries are directed principally at the production of liquids that can be upgraded into transportation fuels or for use as chemical feedstocks. Some of these concepts also yield liquid fuels for use in electric utility or industrial boilers. The level of current development activities for these concepts ranges from bench-scale tests to demonstration plants.

3.3.3.2 Research Needs

Additional R&D activities in this coal refinery category cover several areas. First, additional R&D will better characterize the basic chemical and physical reactions that occur for some concepts. These characterizations should include the influence of coal structure on the liquefaction chemistry. Such characterizations will allow researchers and designers to optimize the concepts to a greater extent than is now possible with many of these concepts. Future R&D activities should include techniques to reduce temperature and pressure conditions in the processing steps, the development of catalysts that are less costly and/or longer lasting, the development of improved chemical solubilization methods, and the influence of coal type on operating conditions and product yields. These and related research activities are presently part of the DOE Coal Liquefaction R&D program.

3.3.4 Bioprocessing Coal Refineries

3.3.4.1 Conclusions

Refinery concepts based on bioprocessing of coal are considerably less developed than most of the concepts considered herein. The experiments are being performed at a very small scale and are addressing fundamental issues such as the type of microorganisms needed, reaction times required, nutrients needed, etc. Although many of these concepts offer a potential for economic operation, the time frame for commercialization is likely much further in the future than most of the other refinery categories.

3.3.4.2 Research Needs

Because of the comparatively early stage of development for this category of refineries, there are basic R&D activities that must be undertaken before these concepts can become commercialized. As noted above, there are several fundamental issues which must be resolved through R&D. Once additional progress has been made in these areas, R&D activities can include greater detail in concept design, concept economics, products yields, and some of the other more conventional aspects associated with the evolution of an R&D process into a commercial entity. There are funda-

mental research activities presently in the DOE Fossil Energy R&D programs related to bioprocessing coal refineries.

3.3.5 General Comments on R&D for Coal Refineries

3.3.5.1 General Conclusions

Of the twenty-seven concepts considered, seven produce electricity as one of their major products. These concepts are principally in the 'devolatilization' and 'gasification' categories. Ten concepts yield a solid product that can be directly burned, slurried into another fuel form, or used as form coke. Twenty-three concepts produce a liquid fuel (including methanol) while seven produce chemical products or intermediates. This range of products illustrates both the flexibility in the use of coal in new markets as well as in the various coal refinery concepts used to process the coal into the appropriate forms. A common objective in the development of these concepts is to obtain the products in a manner consistent with economic competitiveness, energy efficiency, resource utilization, environmental awareness, and national policy.

Coal refinery concepts are in various stages of development ranging from bench or laboratory testing to commercially operational. Proponents include universities, private industry, national laboratories, the Federal Government, and combinations of these.

Several of the concepts discussed in this report have been developed predominately by foreign governments and/or private-industry groups. These concepts have been included not only for comprehensiveness, but to also indicate that foreign competition exists in the development of refinery concepts. Concepts using U.S. technology and expertise must meet this foreign competition as the world strives to expand coal markets and utilization in an efficient, economic, and environmentally responsible manner.

3.3.5.2 Common Research Needs

Several common themes of R&D needs were noted among the coal refinery categories. For example, many of the concepts have been experimentally and/or analytically examined for a limited number of coal types - often only one. To fully evaluate the potential for these concepts for meeting new and expanded markets for coal-derived products, there is a need to determine the impacts of different coals on product yields, characteristics, and overall process efficiency. A second common theme concerns operation of the coal refineries in an integrated system rather than as a collection of individual components. Once again, overall efficiencies and economics will be better estimated when experience with fully integrated systems is gained. A third common theme is for continuing analyses of product demand and prices to assure that the products from these coal refineries will find their niches in the marketplace.

There are several levels of potential R&D for coal refineries. One level is concerned with the basic phenomena or processes that are important to all coal refinery concepts and indeed to all processes involving the use of coal. Areas of R&D that might be important at this level include the basic structure of coal along with its basic reactions with chemicals and reagents or the influence of various catalysts.

A second level of R&D for coal refineries could be more focussed toward a general category of concepts. For example, R&D on catalysts may be applicable to several concepts within the liquefaction category, and research on hot-gas cleanup systems may improve the efficiency and environmental features of several concepts in the gasification category. R&D at this level could apply to concepts in more than one category due to similarities of some of their components. An example here may be R&D on volatile yields, which could help concepts in both the devolatilization and gasification categories.

The third and final level of R&D activities presented here is addressed to a specific process or concept. This level is reached after the concept has undergone extensive evaluation and experimentation and typically involves a large demonstration-scale, near-commercial facility in which many of the individual components of a concept are integrated into a complete system. The ENCOAL Mild Gasification facility being constructed in Gillette, Wyoming as part of the Clean Coal Technology Program is an example of a coal refinery concept that has reached this level of development.

There are several existing R&D programs within DOE at each of these levels. As pointed out in many of the concept descriptions presented in the appendices, several on-going R&D activities are relevant to coal refineries. In general however, the existing R&D activities are directed to general programs under DOE stewardship and not toward any specific coal refinery concept. Of course, those concepts for which the third level of R&D is appropriate, e.g., the ENCOAL concept, have R&D activities that are focussed more directly on them. Because there are existing R&D activities within DOE at all levels and which are applicable to coal refineries, there appears to be little or no need to establish new R&D programs specifically toward coal refineries but rather to continue to support the necessary R&D within the programmatic structure currently in effect in DOE.

REFERENCES

1. *Expanding Non-Utility Applications of Coal*, Unnumbered report by the U.S. Department of Energy, Office of Fossil Energy (June 1988)
2. Conference Report accompanying the FY 1991 Department of Interior and Related Agencies Appropriations Act, p. 113 (Aug. 1990)
3. "Carbonization," in *Encyclopedia of Chemical Technology*, Third Edition, H. F. Mark *et al.* editors, John Wiley & Sons, New York, NY, pp. 284 to 306 (1979)
4. L. A. Munro, *Chemistry in Engineering*, Prentice-Hall Inc., Englewood Cliffs, NJ (1964)
5. *Energy Technologies and the Environment: Environmental Information Handbook*, prepared by Argonne National Laboratory, DOE/EH-0077 (October 1988)
6. J. B. O'Hara *et al.*, "Project POGO - A Coal Refinery", *Chemical Engineering Progress*, Vol. 74, No. 8, pp. 49 to 63 (August 1978)
7. *Great Plains Coal Gasification Plant Public Design Report*, DOE/CH-10088-1874 (July 1985)
8. G. L. Touchton *et al.*, "Coal Refineries - Power Plants for the Future", paper presented at the 1987 American Power Conference, Chicago, IL, April 1987
9. M. Shepard, "Coal Technologies for a New Age", *EPRI Journal*, Vol. 13, No. 1, pp. 5 to 17 (January/February 1988)
10. J. Douglas, "Breaking Through Performance Limits: Beyond Steam", *EPRI Journal*, Vol. 15, No. 8, pp. 4 to 11 (December 1990)
11. D. Boutacoff, "Methanol - A Fuel for the Future?", *EPRI Journal*, Vol. 14, No. 7, pp. 23 to 31 (October/November 1989)

APPENDIX A

DEVOLATILIZATION COAL REFINERY CONCEPTS

CALDERON

Introduction

The Calderon concept is designed to convert the volatile matter of the coal to a clean synthesis gas suitable for production of liquid fuels along with a residual char which is ultimately converted to a fuel gas for electric power generation. The notable differences between the Calderon process and conventional devolatilization technologies which aim for coproduction of liquid fuels and electricity, are that the run-of-mine coal is not pretreated before use (such as by comminution for particle size reduction or moisture removal), air instead of oxygen is used, and the product gases are not cooled before cleanup as required for conventional combined-cycle systems. The product gases are treated to recover elemental sulfur by a proprietary hot gas cleanup process devised by the Calderon Energy Company. The energy content of the coal is not partially converted into steam during a cooling stage (as in a conventional cleanup) but is retained in the product gases undergoing hot gas cleanup.

This process is being advanced by the Calderon Energy Company of Bowling Green, OH, as a potential cost-effective means of producing a clean synthesis gas and fuel gas from run-of-mine high-sulfur coal. These clean gases would be suitable in applications such as methanol production and electric power generation.

A coal refinery concept based on the Calderon process that is somewhat different than the PDU actually being tested is shown in Figure 1. The system depicted integrates the generation of a rich fuel gas for methanol conversion and a lean fuel gas for electric power production. The necessary inputs to this coal refinery include run-of-mine coal, air, water, and make-up lime sorbent, while the major products are methanol and electricity. Elemental sulfur would be a byproduct from this coal refinery.

Detailed Process Description

Unless otherwise specified, this section is a description of the Calderon Process PDU being tested at Alliance, Ohio.

Run-of-mine coal is fed into the Pyrolysis Reactor, where the coal thermally decomposes in the absence of air. The volatile matter of the coal is converted into a product synthesis gas stream (called "rich gas") composed of a mixture of hydrogen, carbon monoxide, carbon dioxide, methane and higher hydrocarbons, water, and vaporized liquid tars (primarily aromatics), and a devolatilized solid char. The devolatilized char is of higher calorific value than the original coal and exhibits properties suitable for utilization in gasification (being porous, and easily friable or broken). The mineral matter within the coal remains with the char.

The required energy for coal pyrolysis is supplied by a portion of the hot gas effluent from the Char Gasifier. The relative yield of liquid tar and gaseous pyrolysis hydrocarbon products will depend on the volatile matter content in the coal, the reaction temperature, and the residence time of the coal particles in the Pyrolysis Reactor.

The rich gas is a medium-Btu synthesis gas with a heating value between approximately 310 to 320 Btu per scf. Desulfurization of the rich gas is accomplished by a proprietary hot gas cleanup system being developed by Calderon Energy Company. This hot gas cleanup system contains a sorbent (lime) bed which in the Calderon PDU is heated along with the rich gas by the hot gas effluent from the Char Gasifier. The combination of heated gas and the presence of a sorbent allows for desulfurization of the rich gas while the higher hydrocarbons in the rich gas are cracked (large molecules converted into smaller molecules) to form carbon (required for regeneration of the sorbent), CO, H₂, and other gases. Carbon is deposited on the spent lime sorbent; this carbon will be used in a later step to regenerate the spent sorbent. The mechanism by which the lime (calcium oxide, CaO) reacts with hydrogen sulfide, H₂S, in the rich gas to form calcium sulfide, CaS, may involve the following reaction:



with the water generated exiting with the cleaned rich gas stream.

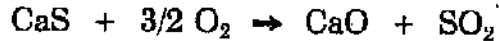
The rich gas composition is shifted to attain a lower ratio of hydrogen to carbon monoxide in the range of 2:1 [1]. The shifted rich gas then passes through the methanol synthesis reactor(s), converting hydrogen and carbon monoxide to methanol. The methanol synthesis reaction is limited by chemical equilibrium so that the exiting methanol concentration is usually less than 7 percent [2]. The product methanol in the effluent gas is recovered by condensation after cooling, with the unreacted gases that remain recycled many times through the methanol synthesis reactor(s).

The char enters the Char Gasifier, which is a slagging downward moving-bed. The char, supplied in lump form, moves downward in countercurrent flow against an ascending stream of the gasifying agent (air), with the ash, stripped of carbon, being discharged from the base of the reactor. The char is rapidly heated in the upper portion of the moving bed by the exiting gasifier product gas and then reacts in the lower portion with the feed air. The temperature at the reactor bottom is maintained above the ash fusion point, with the ash melting and leaving as a liquid slag. Slagging operation has the advantage that the lean gas is virtually free of steam, leading to a reduction in the volume of aqueous liquor in the product gas stream and a gain in overall thermal efficiency [5]. The lean gas can be considered to be a low-Btu gas with an approximate heating value below 130 Btu per scf.

The lean gas exits the top of the gasifier and must be extensively cleaned prior to combustion, both for environmental considerations and for turbine reliability. The hot gas cleanup system for the lean gas is similar to that for the rich gas.

In Figure 1, the lean gas is fired with air in the Gas Turbine, generating electricity. In the PDU, the lean gas is returned to the pyrolyzer to provide heat to the coal and rich gas. As shown in Figure 1, the hot exhaust gases from the Gas Turbine generate steam in the Heat Recovery Boiler, with the steam used to drive the Steam Turbine/Generator, producing additional power.

The sorbent lime from the hot gas cleanup system is regenerated by oxidation with air. During regeneration, air flows through the sorbent bed to react with the sulfur compounds to form SO_2 :



while the carbon deposited on the spent sorbent is removed by partial oxidation with O_2 to form carbon monoxide:



and by oxidation with SO_2 to yield sulfur in elemental form:



The elemental sulfur exits the hot gas cleanup system as a vapor mixed with CO and nitrogen, and is recovered by cooling and condensation [4].

Hot gas cleanup processes promise improved efficiency and process simplification. Cold gas cleanup systems penalize the cycle efficiency and capital costs because the fuel gas has to be cooled for desulfurization and particulate removal, then reheated prior to combustion [3], which requires expensive heat exchange equipment and results in unavoidable energy losses. In combined-cycle applications, hot gas cleanup allows a greater proportion of the coal's energy to be recovered in the gas-turbine cycle, which is thermodynamically more efficient than the steam cycle [6]. The estimated heat rate for combined-cycle operation based on the Calderon process is approximately 8,210 Btu per kWh (41.6 percent thermal efficiency), in comparison with a good pulverized-coal plant with pollution controls to limit sulfur and nitrogen oxide emissions which might have a heat rate as low as 9,300 Btu per Kwh [7].

A coal conversion (based on carbon) of greater than 99 percent has been estimated for this process.

Types of Feed Coal

This process has been designed to primarily process Eastern high-sulfur (in the range of 3.2 percent), caking coal [4]. Caking tendencies of the feed coal may be required so that the devolatilized material resulting from coal pyrolysis will agglomerate into a friable mass before char gasification. Gasification of the coal char is by moving-bed technology, for which special provisions are required for handling fine char (due to possible elutriation of the fine char with the product gases) [5].

Batch operation of the individual system components (pyrolysis, char gasification, hot gas cleanup) has been tested on a bench-scale unit (capacity of 164 pounds coal) with a variety of coals [4].

Products

The main products from this coal refinery concept are methanol and electricity. Reports indicate that the process has the potential to coproduce 0.4 pounds (0.06 gallons) of methanol and 0.67 kWh of electricity from a pound of typical high-sulfur coal (as delivered) [8].

Process calculations predict a sulfur recovery of approximately 99 percent, so that the production rate of marketable (elemental) sulfur would essentially equal the percentage of sulfur in the feed coal [4].

Likely Applications

This coal refinery is an example of a coal refinery in which electric generation is coupled with coproduction of commercial chemicals. Coproduction of electricity and chemical products in such a manner can potentially reduce the cost of electric generation [9]. It would be expected that the most likely commercial entities interested in owning and operating a coal refinery based on the Calderon process would be the electric utility industry or independent power producers. The final application of this coal refinery concept will primarily depend on the successful commercial-scale demonstration of the process, the required capital investment, and the overall process economics.

Status of Development

The separate operations of the Pyrolysis Reactor, Char Gasifier, and Hot Gas Cleanup system have been demonstrated in batch mode processing using batch sizes of 164 pounds of coal. Pyrolysis tests have been also conducted at atmospheric pressure with a variety of coals [10].

A process development unit (PDU) in Alliance, Ohio, has undergone shakedown testing. This PDU, with an operating pressure of 300 psig, is rated at 24 ton per day,

and to date has been restricted to limited production of char, rich and lean gas streams. The PDU has not yet reached total integrated operation status, due to problems with operation of the downstream hot gas cleanup sulfur removal and recovery components. Therefore, testing has not yet been able to establish process feasibility. Testing of the PDU has been limited primarily to operation of the Pyrolysis Reactor and Char Gasifier components. The Pyrolysis Reactor is full-scale commercial design size, and the Char Gasifier is 38 percent of full scale [12]. The PDU was designed to process a high-sulfur Midwestern coal typical of that produced by Ohio mines [8]. The PDU was constructed to establish overall integrated process technical feasibility through integrated operation, test the integration of process controls, establish process performance under pressure operation, and establish the rich and lean gas separation [10].

A 80 MW commercial plant that would coproduce 600 tons per day of methanol from 500,000 tons per year of high-sulfur coal has been proposed as the next level of scale-up [11]. A prototype commercial-scale demonstration plant processing 984 tons of coal per day to produce 414 tons of methanol per day and 80 MW of electricity was submitted in Round 4 of the Clean Coal Technology (CCT) program [13].

Environmental Aspects

The Calderon process can theoretically convert high-sulfur caking coal into a liquid fuel (methanol) low in sulfur and other contaminants, and electricity. The majority of the sulfur and mineral matter within the coal is recovered from the process in the form of marketable elemental sulfur and slag, thereby avoiding potential solid waste disposal concerns. The slag that this coal refinery produces is reported to be inert and nonhazardous.

NO_x emissions from this process are expected to be within the minimum level of control allowed by NSPS because the temperature within the Gas Turbine cycle will be low enough to limit formation of thermal NO_x. The SO₂ emission rate would presumably be in accordance with the minimum level of control allowed by NSPS, as the process reportably removes close to 99 percent of the sulfur in the coal [11].

Wastewater is generated during dewatering of the quenched slag and from steam generation. Minimal production or discharge of wastewater is reported, with potential for zero discharge [8].

Research Needs

This process is complex and involves integration of proprietary process steps whose performance level is unknown (the hot gas cleanup technology). Integration of the many separate process steps resulting in a reliable, efficient and economical unit has not yet been accomplished at PDU scale. Demonstration of the technology at near-commercial scale may warrant further investigation.

The hot gas cleanup technology advanced here is an extension of earlier technologies using limestone or other sorbent. The initial capital investment and overall process economics will depend on the projected sorbent bed life and the degree to which the bed can be regularly regenerated without sorbent degradation. Demonstration of Calderon's proprietary hot gas cleanup technology over a period of many cycles may be warranted to establish the technical and economic viability of the process.

References

1. *Coal Gasification Systems: A Guide to Status, Applications, and Economics*, prepared by Synthetic Fuels Associates, EPRI Research Reports Center, Palo Alto, CA, Report No. AP-3109, pp. 5-153 to 5-154 (June 1983)
2. "Petrochemical Handbook '91," *Hydrocarbon Processing*, Vol. 70, No. 3, p. 164 (March 1991)
3. J. Makansi, "Gasifier Makes Coal-Fired Turbine A Commercial Powerplant," *Power*, Vol. 134, No. 4, pp. 75 to 80 (April 1987)
4. A. Calderon, "Process Development Unit for Coal Gasification Tied to Regenerative Hot Gas Cleanup," *Proceedings of the Seventh Annual Gasification and Gas Stream Cleanup Systems Contractors Review Meeting*, DOE/METC-87/6079, Vol. 2, pp. 537 to 541 (August 1987)
5. *Chemistry of Coal Utilization, Second Supplementary Volume*, M. A. Elliott editor, John Wiley & Sons, New York, NY, pp. 1611 to 1614 (1981)
6. J. Makansi, "Combined-Cycle Powerplants," *Power*, Vol. 134, No. 6, pp. 91 to 126 (June 1990)
7. J. Douglas, "Breaking Through Performance Limits Beyond Steam," *EPRI Journal*, Vol. 15, No. 8, pp. 4 to 11 (December 1990)
8. K. Campbell *et al.*, "Calderon Coal Gasification Process Development Unit Design and Test Program," *Proceedings of the Eight Annual Gasification and Gas Stream Cleanup Systems Contractors Review Meeting*, DOE/METC-88/6092, Vol. 1, pp. 263 to 269 (May 1988)
9. D. Boutacoff, "Methanol, A Fuel for the Future?" *EPRI Journal*, Vol 14, No. 7, pp. 24 to 31 (October/November 1989)
10. "Calderon Hopes Third Time's a Charm," *Coal & Synfuels Technology*, Vol. 10, No. 30, pp. 1 to 2 (August 7, 1990)

11. "Gasification Process Set for Commercialization," *Coal & Synfuels Technology*, Vol. 11, No. 38, p. 8 (October 1, 1990)
12. "Calderon to Run by September," *Coal & Synfuels Technology*, Vol. 11, No. 6, p. 3 (February 12, 1990)
13. "Round 4 Goals Are for Five to 15 Projects," *Coal & Synfuels Technology*, Vol. 12, No. 22, pp. 1 to 3 (June 3, 1991)

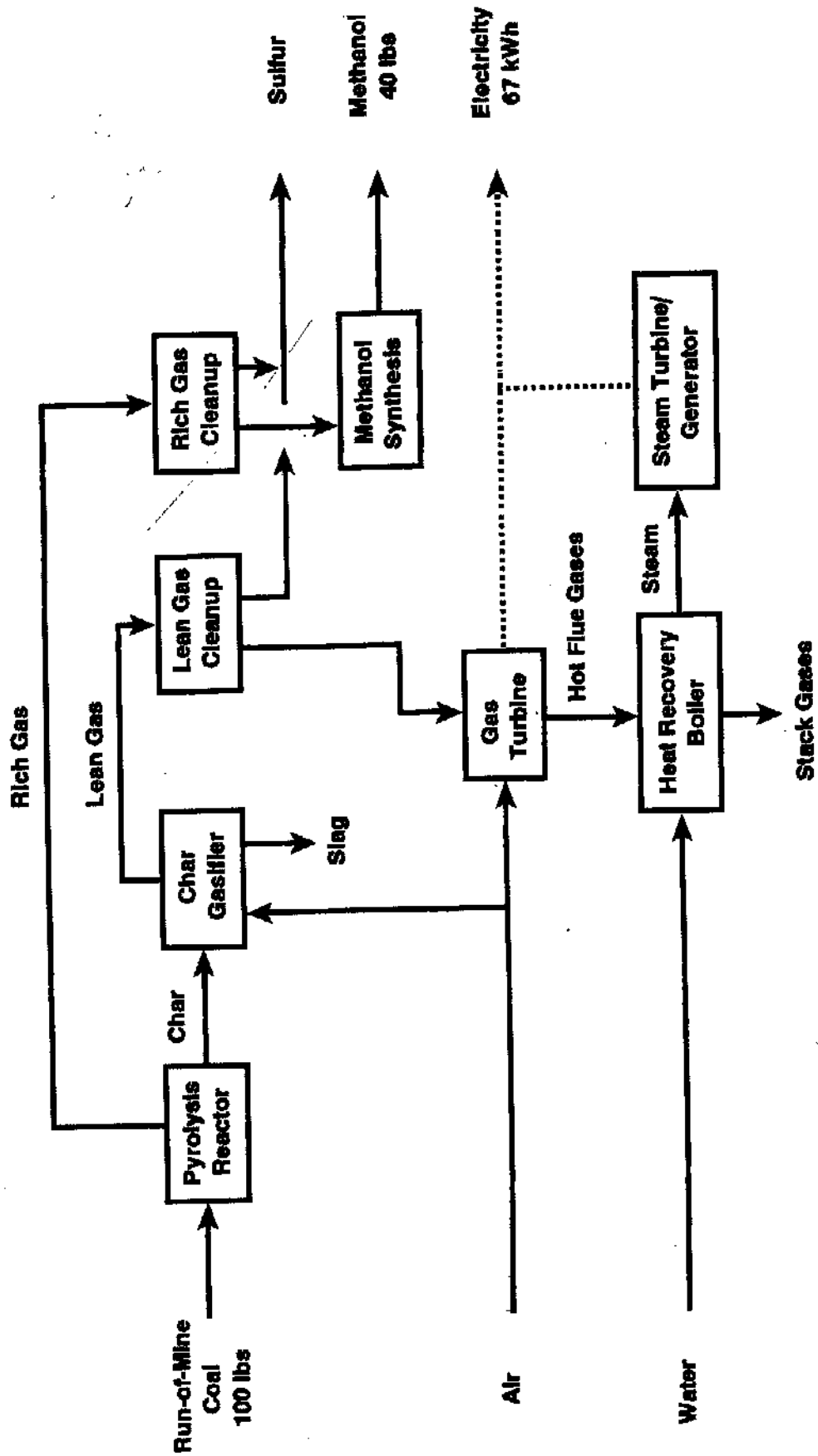


FIGURE 1: Overall Block Diagram of the Calderon Concept

CHARFUEL

Introduction

The Charfuel concept uses a technique called "short-residence time flash hydrodisproportionation (SRT-HDP)." It is effectively the short residence time devolatilization of coal to produce char and liquid co-products while minimizing the production of gas [1]. It is reported that the process utilizes the hydrogen inherent in the coal, eliminating the need for external hydrogen. The SRT-HDP process creates two types of products; one is a char-processed oil/wet methanol slurry (called Charfuel fluidic fuel) with a heating value per pound greater than the parent coal and lower in potential pollutants (sulfur, nitrogen). The second consists of a slate of hydrocarbon liquids (naphtha; benzene, toluene, xylene (BTX); methanol) that are combustible and can be beneficiated (by hydrotreatment) to achieve commercial grade products.

This concept has been proposed by Char-Fuels of Wyoming, Inc., a unit of Carbon Fuels Corp. The process itself is a variation of flash hydro-pyrolysis, in which coal is thermally devolatilized by heating without air.

The Charfuel coal refinery concept is shown in Figure 1. The system concept would integrate a series of commercially-proven processes with two newer processes (HDP reactor and char separator; hydrotreating). The necessary inputs would be dried and pulverized coal, air, electricity, and water, while major products include liquid hydrocarbons and a char-oil slurry. Sulfur, ammonia, and CO₂ would be byproducts of this coal refinery.

Detailed Process Description

This concept would integrate many technologies that are commercially available with a new coal/hot gas injector design for coal hydrodisproportionation and char separation. A detailed flow diagram is given in Figure 1, with all streams based on 100 pounds of as-received coal. The inlet coal would be Western Kentucky No. 9, which is a high-volatile bituminous coal, with a higher heating value of about 12,500 Btu per lb (dry basis) and a sulfur content of 3.0 percent by weight (see Table 1 for more details). The following process description is based on the conceptualized block flow diagram of the Charfuel process depicted in Figure 1.

In the Coal Preparation section, the run-of-mine coal is pulverized to a particle size of 70 percent less than 74 micron and purged by a heated gas stream (150 to 400° F) to partially dry the coal to a moisture content in the range of 2 to 4 percent by weight. The pulverized coal may then be sent to the Pre-Conditioning section, where superheated steam and the methane/carbon monoxide (CH₄/CO) rich gas from the Gas Separation section preheats and preconditions the coal; it has been shown that, depend-

ing on the initial coal characteristics, pre-conditioning of coal with steam can improve the yield and quality of condensable products obtained from coal pyrolysis [2].

The steam/CH₄/CO gas stream from the Pre-Conditioning section enters the Partial Oxidation (POX) unit, together with oxygen from the Air Separation plant. A portion of the N₂ stream from the Air Separation plant is used for process requirements (such as purging, pressurizing), with the remainder vented. Partial oxidation is the reaction of oxygen at high temperature and pressure (2,000 to 2,600° F; 500 to 700 psig) with a molecule that may or may not contain oxygen, resulting in a hot, reducing gas containing H₂, CO and steam, along with CO₂. This hot gas stream enters the HDP reactor to provide the required energy and hydrogen-rich atmosphere for the hydrodisproportionation of the conditioned coal.

Coal from the Pre-Conditioning section is fed into the SRT-HDP down-flow entrained flow reactor. The coal resides in the reactor less than one second and is rapidly heated by contact with the hot POX gas containing hydrogen to volatilization temperatures between 1,200 and 1,700° F at a heating rate between 10⁴ to 10⁵ °F per second [3]. Research has shown that the yield of volatiles from coal increases with heating rate [4]. The coal is hydrodisproportionated to a solid carbonaceous material (char) and a hydrocarbon gas phase. The products are quenched to a temperature of less than 1,000° F using recycled heavy oil to control cracking (conversion of large molecules to smaller molecules) of the heavy unsaturated hydrocarbons to maximize formation of liquid hydrocarbons while minimizing formation of undesired light gases.

The char dust is separated from the hydrocarbon gas phase (HDP vapor) in the Char Separation section. Most of the char (about 88 percent) is then sent to the Char Cooling & Grinding section, where it is ground to a particle size of 32 percent less than 44 micron. The cooled and sized char is mixed with hydrotreated oil (from the Hydrotreating & Fractionation section), "wet" methanol (from the Once-Through Methanol Synthesis & Purification section), and hydrocarbon-containing water, to form a char-liquid slurry (Charfuel Fluidic fuel). The characteristics of the char-liquid slurry are given in Table 2.

A portion of the char from the Char Separation section is sent to the Fluidized Bed Boiler unit, where it is combusted to produce the steam required for pre-conditioning the coal. The treated water used for steam generation comes from the Water Treatment unit.

The hot quenched HDP vapors are then sent to the Cooling Separation section, to where the HDP vapor is cooled in consecutive stages, to condense the water and hydrocarbon liquids. The water and hydrocarbon liquids are separated by an oil-water separator, with the heavier hydrocarbons recycled back to the HDP reactor as oil quench. The condensed light oil is sent to the Hydrotreating & Fractionation section, where the light oils are hydrotreated (elimination of sulfur and nitrogen by the action

of hydrogen under pressure over a catalyst). The resulting liquid may be fractionated to separate the benzene, toluene, and xylene (BTX) from the naphtha. Commercial grade naphtha and BTX products (about 1 ppm sulfur; about 0.1 ppm nitrogen) are recovered, both of which can be used as chemical feedstocks and/or gasoline blending stock.

The water from the Cooling Separation section is stripped of any acid gases and ammonia in the Water Treating section by conventional means (one method is to pass steam through heated water to remove dissolved gases such as ammonia and hydrogen sulfide). The ammonia is then recovered for sale as anhydrous ammonia. The acid gas is sent to the Sulfur Recovery section.

The cooled sour gas contains sulfur compounds (H_2S , COS) that are removed in the Sulfur Removal section. Typically, the sulfur compounds within a sour gas are absorbed by a physical or chemical solvent and concentrated in a gaseous stream. The concentrated sulfur gas stream is then converted into elemental sulfur. The byproduct off-gases from the elemental sulfur recovery section are then processed. For this example, the physical absorption of sulfur is accomplished in the Gas Purification section by a Rectisol[®] acid gas removal unit, with a Claus[®] sulfur recovery unit to convert the gas stream into elemental sulfur, and a SCOT process for off-gas treatment [5]. Approximately 99.5 percent of the sulfur in the sour gas stream is recovered. The elemental sulfur can be sold in the commercial market. The Rectisol[®] unit also removes CO_2 to a level of approximately 3 percent, so that the resultant gas can be used for methanol synthesis (using conventional technology) without appreciable formation of water. The CO_2 may be stored and compressed to 1,500 to 2,000 psig for possible pipeline delivery.

The purified gas then passes through the Once-Through Methanol Synthesis process, where a portion of the coal-derived gas is converted to crude methanol. Crude methanol may contain up to 10 to 25 percent by weight of water, depending on the feedstock, with approximately 1500 ppm of higher alcohols [6]. The condensed crude methanol which contains water and trace amounts of organics is stripped of the light organics and separated by distillation into a pure methanol stream and a methanol-rich water stream. The methanol-rich water stream is not distilled any further to recover the methanol, but is sent to the Slurry Preparation section for inclusion in the Charfuel fluidic fuel.

The non-condensable purge gas is separated into a H_2 -rich stream and a hydrocarbon-rich (primarily CO and CH_4) stream in the Gas Separation section. The H_2 -rich stream is used to satisfy process needs, while the hydrocarbon-rich stream is primarily used as feed to the POX unit.

Types of Feed Coal

Short-residence time hydrodisproportionation converts the solid volatile matter in a carbonaceous material to char and volatilization products.

To date, most research on the Charfuel process has centered on Western Kentucky No. 9 bituminous and Powder River Basin subbituminous coals. Current research is being conducted on Glenrock (Wyoming) coal [7].

The physical properties of the coal can affect the performance of this coal refinery. Coals of lower volatile content will not produce a large enough amount of liquid hydrocarbons sufficient for slurring of the Charfuel Fluidic fuel so that alcohols or other hydrocarbons will have to be added. Also, coals of higher rank will negatively affect the HDP process due to possible agglomeration and slaking (crumbling) caused by coal swelling; the plasticity of the coal particles would inhibit volatilization of the solid organic material in the coal.

Products

The main products from this example coal refinery are a char-liquid slurry, methanol (CH_3OH), naphtha, and BTX. Marketable byproducts can include (elemental) sulfur, carbon dioxide (CO_2), and ammonia (NH_3). The product output is given in Table 3 in terms of pound product per pound of feed coal (as received). This analysis shows that approximately 0.61 pounds of Charfuel fluidic fuel, 0.04 pounds of methanol, 0.01 pounds of naphtha, and 0.04 pounds of BTX are produced from one pound of coal (as received).

The product distribution is dependent on the type of feed coal (due to the amount of volatiles, initial moisture content, free swelling index, and other coal characteristics). The product output for a Powder River Basin subbituminous coal is shown in Table 4, with the coal characteristics given in Table 5.

Likely Applications

Naphtha is an intermediate in petroleum refining and can be further treated to produce high octane reformat, for blending in motor gasoline or as a petrochemical feedstock. BTX is a valuable chemical feedstock and fuel additive.

The Charfuel fluidic fuel can be substituted for coal or fuel oil for boiler applications. It has certain advantages over the parent coal in that it has a lower sulfur and nitrogen content, is more uniform, has physical properties similar to low density (petroleum-based) fuel oils, and can be more easily stored and transported.

One primary application to service the electric utility market that had been proposed in the past was to fire the 100-MW No. 1 unit at the Dave Johnson power plant in Glenrock, WY with the Charfuel Fluidic slurry from a 1,000 ton per day Charfuel plant [3].

Status of Development

The short residence time hydrodisproportionation (SRT-HDP) reactor system has been tested at bench-scale by the Carbon Fuels Corporation, using coal flowrates of approximately 5 lb per hour. The components in the SRT-HDP reactor are presumed to be similar to other SRT reactor systems which have been tested by others at coal flowrates of up to 24 tons per day [4, 8]. A bench-scale study was undertaken by the Western Research Institute to confirm the reaction chemistry, and verify yield data generated by other investigators in flash hydrolysis. A bench-scale optimization study for the demonstration project (about 5 lb per hour of dry Glenrock coal) is currently underway [7]. A "cold flow" study by Western Research Institute in a 150 ton per day test unit commenced in mid-March 1991. The objective of the study is to provide hydrodynamic mixing data required to verify the coal feed system and the coal/hot gas injector nozzle performance of the SRT-HDP reactor system that will be part of a demonstration facility to be constructed at Glenrock, Wyoming [7].

A prototype demonstration-scale plant processing 150 tons of coal per day to produce oil and char (for potential firing in a 100 MW boiler) was submitted in response to the fourth solicitation of the Clean Coal Technology (CCT) program [9].

Environmental Aspects

It is stated that the Charfuel process extracts the majority of the sulfur and nitrogen from the parent coal in the form of elemental sulfur and ammonia. Because approximately 85 percent of the sulfur and 65 percent of the nitrogen are removed from the raw coal, it can be expected that the Charfuel Fluidic fuel can be burned in boilers designed for coal while generating much lower SO₂ and NO_x emissions [12].

The main environmental intrusions from this coal refinery include atmospheric emissions of SO₂ and NO_x (from the combustion of a portion of the char to generate steam), and solid wastes. The emission rate for SO₂ would be on the order of 0.0001 lb per lb of feed coal (for Western Kentucky No. 9, and assuming 90 percent sulfur capture within the AFBC; approximately 0.008 lb SO₂ per million Btu), while for NO_x, it would be less than 0.0001 lb per lb of feed coal. The SO₂ and NO_x emission rates would meet the limits allowed by the NSPS.

The average solid waste production rate would be on the order of 0.05 lb per lb of feed coal, and would include the ash from the char used for steam generation and spent sorbent (in the form of calcium sulfate, calcium carbonate, etc.). It would be

expected that the toxicity of the solid waste would not differ greatly from that generated from a coal-fired power plant.

Research Needs

The market price of the Charfuel Fluidic fuel would be enhanced if it could be beneficiated (to remove the ash and sulfur content). This would entail research along this line to determine the degree of char cleaning required and its effect on the process economics.

Bench scale experiments are being performed to prove the technical aspects of the hydrodisproportionation and hydrotreatment processes. Additional bench-scale testing, followed by demonstration at a larger PDU scale may be warranted to assure sufficient data to assess the potential of this concept for commercial-scale demonstration.

The reaction kinetics and chemistry of the Charfuel process are as yet not completely established. Application of the Charfuel process to other types of coals may warrant process development work to determine possible avenues of optimization.

Table 1: Analysis of Coal Used in Example Charfuel Plant Feed

ULTIMATE ANALYSIS (weight percentage, dry basis)					
Carbon	Hydrogen	Nitrogen	Sulfur	Oxygen	Ash
75.4	5.4	1.2	3.0	7.0	8.0
Free Moisture (wt percent)			8.6		
Higher Heating Value (dry basis)			12,500 Btu per lb		

Table 2: Characteristics of the Charfuel Fluidic Fuel

CONSTITUENTS IN CHARFUEL FLUIDIC FUEL (weight percentage)				
Char	Process Oil	Wet Methanol ^(a)	Sulfur	Nitrogen
50 to 60	25 to 35	5 to 15	0.5 to 0.6	0.6
Heating Value		approx. 13,000 Btu per lb		

(a) contains methanol plus water

Table 3: Product Output from Example Charfuel Coal Refinery

PRODUCT OUTPUT (lb product per lb coal, as received)	
Charfuel fluidic fuel	0.61
Methanol	0.04
Naphtha	0.01
BTX (benzene, toluene, xylene)	0.04
Sulfur, elemental	0.02
Ammonia, NH ₃	0.005

Table 4: Product Output from Charfuel Coal Refinery, Powder River Basin Coal

PRODUCT OUTPUT (lb product per lb coal, as received)	
Charfuel fluidic fuel	0.42
Methanol	0.02
Naphtha	0.02
BTX (benzene, toluene, xylene)	0.03
Sulfur, elemental	0.003
Ammonia, NH ₃	0.004
MTBE	0.03
Carbon Dioxide, CO ₂	0.29

Table 5: Proximate Analysis of Powder River Basin Coal

PROXIMATE ANALYSIS (weight percentage)			
Volatile Matter	Fixed Carbon	Ash	Moisture
31.0	33.3	5.2	30.5
Nitrogen Content (weight %, dry basis)		1.0	
Sulfur Content (weight %, dry basis)		0.5	
Higher Heating Value (dry basis)		8,200 Btu per lb	

References

1. L. G. Meyer, B. C. Sudduth, and G. F. Cavaliere, "Method of Refining Coal by Short Residence Time Hydrodispropyrolsis to Form a Novel Coal Refined Fuel System," U.S. Patent No. 4,938,782; assigned to Carbon Fuels Corp., Englewood, CO (July 3, 1990)
2. R. A. Graff, P. Zhou, and S. D. Brandes, *Steam Conditioning of Coal for Synfuels Production*, prepared by City College of the University of New York, DOE/MC/23288-2697 (November 1988)
3. "Char-Fuels Gets More Money for Clean Coal," *Coal & Synfuels Technology*, Vol. 9, No. 18, pp. 1 to 2 (May 9, 1988)
4. D. F. Tatterson, K. K. Robinson, T. L. Marker, and R. Guercio, "Coal Flash Pyrolysis in a Free-Jet Reactor," *Ind. Eng. Chem. Res.*, Vol. 27, No. 9, pp. (1988)
5. C. H. Taylor, "The Purification of Gases Derived From Coal," Chapter 3-13 in *Handbook of Synfuels Technology*, R. A. Meyers editor, McGraw-Hill Book Company, New York, NY, pp. 3-251 to 3-267 (1984)
6. P. L. Rogerson, "The ICI Low-Pressure Methanol Process," Chapter 2-2 in *Handbook of Synfuels Technology*, R. A. Meyers editor, McGraw-Hill Book Company, New York, NY, pp. 2-45 to 2-73 (1984)
7. "Charfuel to Clean Up Coal's 'Dirty' Image?" *Coal & Synfuels Technology*, Vol. 12, No. 10, pp. 3 to 4 (March 11, 1991)
8. *Technical and Economic Assessment of the Occidental Flash Pyrolysis Process*, prepared by Occidental Oil Corp., EPRI Research Reports Center, Palo Alto, CA, Report No. AP-3786 (December 1986)
9. "Round 4 Goals Are Five to 15 Projects," *Coal & Synfuels Technology*, Vol. 12, No. 22, pp. 1 to 3 (June 3, 1991)

