TECHNICAL REPORT

September 1 through November 30, 1994

Project Title: **PRODUCTION OF LOW-SULFUR BINDER PITCH FROM HIGH-SULFUR ILLINOIS COALS**

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 Principal Investigator: Richard A. Knight, Institute of Gas Technology
 Project Manager: Dan Banerjee, Illinois Clean Coal Institute

ABSTRACT

The objective of this project is to produce electrode binder pitch with sulfur content below 0.6 wt% from high-sulfur Illinois coal mild gasification liquids. In previous ICCI projects at IGT, flash thermocracking was used to successfully upgrade the physical and macromolecular properties of mild gasification pitch. The method yields a suitable blending stock for use as a binder in the production of carbon electrodes for the aluminum industry. However, in pitches from high-sulfur (4%) Illinois coal, the finished pitch sulfur content is still unacceptably high at about 2%.

In this project, two approaches to sulfur reduction are being explored in conjunction with thermocracking: (1) the use of conventionally cleaned coal with low (~1%) sulfur as a mild gasification feedstock, and (2) direct biodesulfurization of the liquids prior to thermocracking. In Case 1, the crude pitch is being produced by mild gasification of IBC-109 coal in an existing IGT bench-scale reactor, followed by distillation of the scrubbing solvent and light-to-middle oils to isolate the crude pitch. In Case 2, the crude pitch for biodesulfurization is the same material previously studied, which was obtained from Illinois No. 6 coal tests conducted in the IGT mild gasification PRU in 1990. Biodesulfurization is to be performed by contacting the pitch with *Rhodococcus Rhodochrous* either as live cultures or in the form of concentrated biocatalyst.

Following preparation of the crude pitches, pitch upgrading experiments are to be conducted in a continuous flash thermocracker (FTC) constructed in previous ICCI-sponsored studies. The finished pitch is then characterized for physical and chemical properties (density, softening point, QI, TI, coking value, and elemental composition), and compared to typical specifications for binder pitches.

This quarter, 45 kg of IBC-109 coal was obtained and sized to 40×80 mesh for mild gasification. Laboratory experiments were conducted to identify means of dispersing or emulsifying pitch in water to render it accessible to biocatalysts, and exploratory desulfurization tests on one-gram pitch samples were begun.

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EXECUTIVE SUMMARY

The objective of this program is to investigate the production of electrode binder pitch with less than 0.6 wt% sulfur from mild gasification liquids. The IGT MILDGAS process produces char, gases, and liquids, which are to be upgraded to: form coke, fuel gas, chemical feedstocks such as BTX and phenols, and industrial pitch binders. From the mild gasification liquids, the 400°C+ distillation residue (crude pitch) comprises 40 to 70% of the total liquid product, representing up to 20 wt% of the *maf* feed coal, but this crude pitch must be upgraded to meet the physicochemical specifications for binders.

The largest market for pitch made from coal liquids is the aluminum industry, which consumes 0.45 kg of anode carbon per kg of aluminum produced. The anodes are typically made by blending 15-35% hot pitch with petroleum coke or pitch coke and heating to a solid graphitized mass. The anodes are continuously consumed, so the industry needs a steady supply of good-quality pitch and filler.

In current practice, electrode binder pitch, valued at \$230-\$275/tonne, is made exclusively from by-product coke-oven tars. The specifications for binder pitch are written purposely to exclude other materials such as asphalt, unmodified low-temperature coal tars, or even substandard coke-oven tars. Pitches from low-temperature tars have not been regarded as suitable for electrode binders, primarily because of inadequate aromaticity and high heteroatom content which lead to unsuitable rheology, reactivity, and resulting physical properties of the baked electrodes. However, because a continuing decline in U.S. metallurgical coke production threatens the supply of by-product coal tar pitch for the aluminum industry, this effort to modify mild gasification pitch for the electrode market offers an opportunity for new uses of Illinois coals.

The process under study in this project is predicated on the benefits of flash thermocracking (FTC) of atomized pitch to achieve desirable pitch properties. In previous ICCI-sponsored projects, we were successful in upgrading the mild gasification pitch to perform satisfactorily as an electrode binder.¹ This was verified not only by the pitch properties (density, softening point, quinoline insolubles (QI), toluene insolubles (TI), coking value, and elemental composition), but also by producing and evaluating test electrodes using the MILDGAS-derived binder pitch and conventional petroleum coke aggregate. The test electrodes met or exceeded all of the specifications for thermal, electrical, chemical, and physical properties used by a major aluminum producer for prebaked aluminum smelter anodes. However, when the parent coal was a high-sulfur (4 wt%) Illinois No. 6, the finished binder pitch still contained more than 2% sulfur, compared to a typical sulfur content of 0.6 wt% for conventional binder specification pitch.

¹ Knight, R. A. 1994. Upgrading Mild Gasification Liquids to Produce Electrode Binder Pitch. Final Report to Illinois Clean Coal Institute, Carterville, IL.

In the current project, we intend to investigate methods to reduce the pitch sulfur. Two sulfur reduction methods are being explored in conjunction with thermocracking:

- (1) Direct biodesulfurization of the liquids before thermocracking, by incubating IGTS8 cell preparations with mild gasification liquids at 30°C and ambient pressure; and
- (2) The use of a conventionally cleaned coal with low (~1%) sulfur (IBC-109) as the mild gasification feedstock.

The biodesulfurization of mild gasification liquid fractions has been previously investigated and shown to be technically feasible.² The test material for biodesulfurization is a crude pitch obtained from MILDGAS PRU tests with Illinois No. 6 coal in April-May, 1990. Following a Gibbs assay of the biodesulfurization activity of the IGTS8 culture to be used, one-gram samples of the crude pitch are emulsified and incubated with the cells at 30°C and ambient pressure for 16 hours. The treated pitch is then extracted with dichloromethane and analyzed for sulfur content. If the results with one-gram samples prove satisfactory, a large (300g) batch will then be desulfurized in the same manner, which will yield a crude pitch sample large enough to be upgraded in the existing FTC unit.

With regard to approach (2), it has been demonstrated by IGT in a previous ICCI-sponsored project that pyritic sulfur is responsible for a significant portion of the organic sulfur in mild gasification coal liquids.^{3,4} This suggests that the mild gasification of a coal with reduced pyritic sulfur could substantially reduce the amount of sulfur in the pitch recovered from the mild gasification liquids. Physical cleaning methods to remove most pyritic sulfur are near maturity, and may be particularly suitable for value-added applications such as processing coal into multiphase products by mild gasification. Test pitch is to be produced from IBC-109 coal in an existing IGT mild gasification reactor, and the resulting crude pitch will then be upgraded in the existing FTC unit.

Pitch Biodesulfurization

In the first quarter, laboratory-scale experiments were performed to identify means of dispersing/emulsifying crude pitch in water to render it accessible to biocatalysts, and to determine the feasibility of biodesulfurization of this material. Dispersion of crude pitch in water was attempted by first freezing the pitch at -70°C, cracking it into millimeter-size fragments, and shaking it in water for 24 hours at 30°C. When this was unsuccessful, experiments were performed using surfactants that had previously been shown to be

² Kilbane, J.J. 1993. Biodesulfurization of Mild Gasification Liquid Products. Final Report to Illinois Clean Coal Institute, Carterville, IL.

³ R.A. Knight, G.J. Koncar, and S.P. Babu. 1991. "The Fate of Sulfur in Mild Gasification Liquids", in *Proc. 1991 Int'l Conf. on Coal Science*, Newcastle-Upon-Tyne, UK, pp. 512-515. Butterworth-Heinemann Ltd., Oxford.

⁴ R.A. Knight, G.J. Koncar, and S.P. Babu. 1990. Mild Gasification Studies with Illinois Coals. Final Report to Illinois Clean Coal Institute, Carterville, IL.

compatible with biodesulfurization catalysts. Reasonably good dispersion/emulsification of pitch was obtained by heating the pitch, thoroughly blending in surfactants, and then adding the mixture to water, followed by shaking for several hours. A final surfactant concentration of 0.5% was required.

Preliminary biodesulfurization experiments were then performed using two methods: (a) incubating emulsified crude pitch with concentrated cell preparation (biocatalyst) for 16 hours at 30°C, and (b) growing *Rhodococcus rhodochrous* IGTS8 under conditions in which crude pitch is the only source of sulfur. For experiments employing concentrated cell suspensions, IGTS8 cells were grown in 10L fermenters using BSM medium containing 0.1% glycerol as a carbon source and 1mM DMSO as a sulfur source. The desulfurization activity of the method (a) cell preparation as measured by the Gibbs assay indicated that the amount of biocatalyst present in this experiment could theoretically remove as much as 160% of the sulfur in the pitch sample treated, so that substrate accessibility was the limiting parameter.

For method (b), experiments were performed to see if IGTS8 could grown in BSM glycerol medium with MILDGAS pitch as the sole source of sulfur. Laboratory-scale shake flask tests demonstrated that IGTS8 could indeed utilize MILDGAS pitch as a sulfur source, but 7 days of incubation at 30°C were required before significant growth was observed. Growth was coincident with dispersion of the pitch, presumably attributable to bioemulsifiers produced by IGTS8. Similar growth tests indicated that IGTS8 is unable to utilize MILDGAS pitch as a carbon source. following the successful results obtained in these preliminary growth tests, additional growth tests were performed using one and two gram samples of pitch and in the presence or the absence of 0.1% non-ionic surfactant. Sterile controls were also prepared and processed similarly. After two weeks of incubation at 30°C, the pitch was recovered by centrifugation and extraction with dichloromethane.

The treated samples from both biodesulfurization methods were submitted for analysis to determine sulfur and carbon values, which will be reported next quarter.

Pitch from Low-Sulfur Conventionally Washed Coal

A 45-kg batch of IBC-109 coal was obtained from the IBCSB. The coal was then crushed and double-screened to 40×80-mesh and riffled to obtain representative sub-samples. The bench-scale mild gasification unit is being prepared for production of crude pitch.

Next quarter, the results of biodesulfurization screening experiments will be reported, biodesulfurization of a 300-g crude pitch batch will begin, and production of a large batch of crude pitch by mild gasification of IBC-109 coal will begin.

OBJECTIVES

The ultimate goal of this project is to develop a method for thermal cracking of MILDGAS crude pitch to produce an electrode binder pitch. The specific objective of the current 12-month project is to reduce the pitch sulfur to a level (0.6%) comparable to that of conventional high-quality binder pitches made from coke-oven by-product tars. Two sulfur reduction methods are being explored in conjunction with thermocracking:

- (1) Direct biodesulfurization of the crude pitch before thermocracking, by incubating IGTS8 cell preparations with crude pitch at 30°C and ambient pressure for 16 hours; and
- (2) The use of a low-sulfur conventionally washed coal such as IBC-109 as the mild gasification feedstock.

The task structure of the current year is as follows:

Task 1. Coal Preparation

Task 2. Preparation of Coal Liquids

Subtask 2.1. Mild Gasification of IBC-109 Coal

Subtask 2.2. Biodesulfurization of Mild Gasification PRU Crude Pitch

Task 3. Flash Thermocracking Screening Tests

Task 4. Test Data Analysis and Interpretation

Task 5. Management and Reporting

INTRODUCTION AND BACKGROUND

Coal tar pitch is used extensively as a feedstock for the production of binding agents employed in carbon and graphite electrodes. The electrodes, composed of approximately 70% coke or graphite filler, 30% binder, and small amounts of lubricants, impregnating agents, or other additives, are consumed in electrolytic smelting of aluminum and steel. The binder serves to plasticize the blend and to cement the solid carbon particles during the carbonization (or graphitization) process. To qualify as electrode binder, the pitch must be a thermoplastic material capable of thoroughly wetting and cementing the filler particles. In addition, the carbonization or graphitization process must result in a high coke yield for the binder.

The largest market for pitch made from coal liquids is the aluminum industry, which consumes 0.45 kg of anode carbon per kg of aluminum produced. The next largest existing market is roof binders, which compete successfully with petroleum-based bitumens, but do not command the premium price of electrode pitch. There are other markets for pitch, but these are relatively small and geographically scattered.

In current practice, electrode binder pitch is made exclusively from high-temperature (980°C+) coke-oven tars. The specifications for binder pitches are written specifically to exclude other materials such as asphalt, unmodified low-temperature coal tars, or even substandard coke-oven tars. A highly aromatic feedstock is required to achieve good physical and chemical stability in the electrode.

Unmodified low-temperature tar pitches have not been regarded as suitable for direct use as electrode binders, primarily because of inadequate aromaticity and high heteroatom content which lead to unsuitable rheology, reactivity, and resulting physical properties of the baked electrodes. Few efforts have been made to modify the chemical and macromolecular structure of low-temperature pitches to achieve the desired properties, primarily because there is no longer a large low-temperature carbonization industry in most industrialized nations where aluminum smelters operate. However, a continuing decline in metallurgical coke production threatens the supply of by-product coal tar pitch for the aluminum industry. Consequently, this effort to investigate methods of modifying mild gasification pitch to meet these specifications offers an opportunity for new uses of Illinois coals.

Mild gasification is an advanced coal carbonization process that emphasizes simple reactor and process design and low-severity processing conditions to bring a slate of value-added co-products (char, fuel gas, and oils/tars) to the marketplace. With support from the U.S. DOE, a project team consisting of Peabody Holding Company, Bechtel National, and IGT has completed a technology development program including the design, construction and

operation of a 45-kg/h PRU.^{5,6,7,8} The MILDGAS reactor consists of a coaxial fluidized-bed/entrained-bed vessel which can process all types of coals. IGT has completed 47 MILDGAS tests on four coals in the PRU, at temperatures ranging from 560°C to 750°C. IGT is currently participating with Kerr-McGee Coal Corporation in the design, construction, and operation of a 24-ton/day MILDGAS process development unit (PDU) at the Coal Development Park operated by Southern Illinois University at Carbondale.

Binder pitch for electrodes used in the aluminum industry has a high market value (over \$270/tonne), and the market is large enough to absorb a new source of raw material. However, it is necessary to modify the tars produced in the MILDGAS process to make them suitable for this use. This can be achieved by raising the temperature of the tar in the vapor phase to achieve thermal cracking. If a thermal treatment is performed on the condensed liquids rather than on the entire effluent stream, the amount of material handled can be reduced by over 50%. This will reduce the heat load for the thermal cracker, lowering capital and operating costs of the process.

In previous ICCI-sponsored work at IGT, flash thermocracking with atomization of the pitch feed was shown to improve most of the key properties of pitch derived from mild gasification liquids. These projects served to determine the operating conditions of temperature, pitch residence time, pitch:gas loading, and gas atmosphere required to produce a pitch with adequately increased QI, TI, coking value, softening point, and carbon content to qualify as electrode binder pitch; and determine the yields of finished pitch and other by-products such as coke, oils, and fuel gas. The ability of the finished pitch to perform as a binder for aluminum smelter anodes was confirmed by producing test anodes. These anodes were comprehensively characterized by Alcoa with respect to strength, density, resistivity, thermal properties, elasticity, permeability, and reactivity to CO₂ and air. The anodes produced from thermocracked MILDGAS-derived pitch were equal or superior to anodes produced from conventional pitch in every characteristic.

However, the sulfur content of the pitch, which naturally results from the processing of high-sulfur coals, is still too high. Users of coal tar pitch for electrode binders generally

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- ⁵ Wootten, J.M., *et al.* 1988. Development of an Advanced, Continuous Mild Gasification Process for the Production of Co-Products. Task 1 Topical Report to DOE/METC, Contract No. DE-AC21-87MC24266.
 - ⁶ Knight, R.A., *et al.* 1990. Development of an Advanced, Continuous Mild Gasification Process for the Production of Co-Products. Task 2 Topical Report to DOE/METC, Contract No. DE-AC21-87MC24266.
 - ⁷ Carty, R.H., *et al.* 1990. Development of an Advanced, Continuous Mild Gasification Process for the Production of Co-Products. Task 3 Topical Report to DOE/METC, Contract No. DE-AC21-87MC24266.
 - ⁸ Knight, R.A., *et al.* 1990. Development of an Advanced, Continuous Mild Gasification Process for the Production of Co-Products. Task 4 Topical Report to DOE/METC, Contract No. DE-AC21-87MC24266.

require a sulfur content no higher than 0.6 wt%, which is typical of a conventionally derived pitch from Eastern coking coals. The thermocracked MILDGAS-derived pitch still contained about 2.0 wt% sulfur. This project aims to develop two methods to produce a binder pitch from high-sulfur Illinois coal that can meet the desired level of 0.6 wt% sulfur:

- (1) Direct biodesulfurization of the liquids before thermocracking, by incubating IGTS8 cell preparations with mild gasification liquids at 30°C and ambient pressure; and
- (2) The use of a low-sulfur conventionally washed coal (IBC-109) as the mild gasification feedstock.

Pitch Biodesulfurization

In a previous ICCI-sponsored project conducted by IGT, the feasibility of biodesulfurization to upgrade the quality of mild gasification liquids, utilizing the ability of *Rhodococcus rhodochrous* IGTS8 to selectively cleave carbon-sulfur bonds, was investigated.² It was shown that the middle distillate (360°-440°F) fraction of liquids derived from the mild gasification of coal, and unfractionated liquids can be biodesulfurized. Moreover, it was demonstrated that lysed cell preparations and freeze-dried cells can be used to biodesulfurize these liquids, as well as unfractionated mild gasification liquids. The importance of the finding that freeze-dried biocatalysts can be used to biodesulfurize mild coal gasification liquids is that freeze-dried cells can be produced at one location, stored indefinitely, and then shipped (at reduced weight, volume, and cost) to another location for coal biodesulfurization. Moreover, freeze-dried biocatalysts can be added directly to mild coal gasification liquids with only minimal additions of water so that reactor volumes can be minimized.

Pitch from Low-Sulfur Conventionally Washed Coal

With regard to the second approach, it has been demonstrated by IGT in a previous ICCI-sponsored project that pyritic sulfur is responsible for a significant portion of the organic sulfur in mild gasification coal liquids.^{3,4} This suggests that the mild gasification of a coal with reduced pyritic sulfur could substantially reduce the amount of sulfur in the pitch recovered from the mild gasification liquids. Physical cleaning methods to remove most pyritic sulfur are near maturity, and may be particularly suitable for value-added applications such as processing coal into multiphase products by mild gasification.

The selected test coal, IBC-109, is a Herrin (No. 6) coal from a Southern Illinois prep plant which has been conventionally washed and contains only 1.1 wt% sulfur, of which 0.6 wt% is organic sulfur.

EXPERIMENTAL PROCEDURES

Task 1. Coal Preparation

Approximately 45 kg of the test coal are to be obtained from the IBCSB, crushed and dried if necessary, sized to 40×80 mesh (180-425 μ m), and stored under nitrogen atmosphere until used. The oversize (+40 mesh) portion will be retained for producing starter char in a fixed-bed carbonizer.

Task 1.2. Preparation of Coal Liquids

Subtask 1.2.1. Mild Gasification of IBC-109 Coal

Coal liquids are obtained from the IBC-109 test coal by mild gasification of the 40×80 mesh coal under N₂ in a mini-bench fluidized-bed reactor (MBFBR). The MBFBR is a continuous-feed fluidized-bed reactor constructed from nominal 2-inch Sch80 316SS pipe with a 4.98-cm i. d. A schematic diagram of the MBFBR unit is shown in Figure 1.

Figure 1. SCHEMATIC DIAGRAM OF MINIBENCH FLUIDIZED-BED REACTOR

Preheated fluidizing gases enter the reactor through a perforated 316SS disk at the reactor bottom. Coal is fed into the fluidized bed through a nominal 1-inch pipe by means of a variable speed feed screw. The feed point is 2.5 cm above the gas distributor. Coal:char mixtures are fed into this section, where a portion of the fluidizing gas sufficient to maintain rapid dispersion of the fresh coal into the char bed is introduced. The bed height is set by selecting one of three overflow ports which are located 13, 18, and 23 cm above the gas distributor. A nominal 4-inch disengaging section is located 91 cm above the distributor plate. A porous 316SS cartridge filter separates entrained fines from the hot gas stream at the top of the disengaging zone. A thermowell extends from the top flange of the reactor to the fluidization plate, with thermocouples located at various heights for accurate bed temperature monitoring.

In a typical MBFBR mild gasification run, a blend of coal and char, the ratio dependent on the coal caking properties, is fed at a controlled rate into the fluidized bed. Coal char produced from the IBC-109 coal in a separate fixed-bed carbonizer reactor is used as a diluent to prevent caking of the coal. It is also important to screen the coal thoroughly to remove fines (-80 mesh), which strongly promote agglomeration. The optimal coal particle size is 40×80 mesh (180-425 μ m). In the case of the test coal to be used in this project, the selected coal content of the feed mixture is 20 wt% for a feed rate of about 10 g/min. The bed is fluidized by preheated nitrogen, with the gas flow regulated by a mass flow controller. The filtered effluent stream passes through a series of condensers, impingement filters, and knockouts to remove tars, oils, and water. A quench solvent, dichloromethane, is injected to aid in coalescing and scrubbing out the tar aerosol. Exit gas samples are obtained, and the exit gas volume measured at regular intervals before the gas stream is scrubbed of H₂S in a molecular sieve tower. Overflow char is collected in a purged lock-hopper system. Essential instruments are located in a remote panel.

The mild gasification conditions are nominally 590°C, 2.4 atm, solids residence time 40 min. Five passes are to be performed, feeding 4.7 kg of coal:char mixture per test. This produces a total of at least 740 g of coal liquids from 3.7 kg of fresh IBC-109 coal. The liquids from the gasification are condensed and subjected to a preparative distillation to remove low-boiling components up to approximately 260°C. The resultant crude pitch, amounting to about 375 g, is a solid at room temperature.

Subtask 1.2.2. Biodesulfurization of Mild Gasification PRU Crude Pitch

A crude pitch previously produced by the mild gasification of Illinois No. 6 coal in the IGT MILDGAS process research unit (PRU) is subjected to biodesulfurization using *Rhodococcus rhodochrous* IGTS8, either as live culture or as freeze-dried cells. The crude pitch was produced during a previous U.S. DOE project, in April-May, 1990.⁸ The parent coal was Illinois No. 6 seam coal from Peabody's Baldwin No. 1, Marissa, and River King No. 6 mines. The effluent oils/tars were collected in a xylene quench tower and subjected to a preparative distillation to remove solvent and low-boiling components up to approximately 260°C. The materials from three MILDGAS tests (IST-5, IST-7, and IST-9) were combined to yield a 9-kg composite sample. These three PRU tests were all

operated at nearly identical conditions of $599 \pm 3^\circ\text{C}$, 1.68 atm, 11 ± 2 min solids residence time, in a 100% N_2 fluidizing atmosphere. The feedstock was a 1:1 (w/w) mixture of Illinois No. 6 coal and recycled char from previous PRU tests.

The biodesulfurization activity of various biocatalyst preparations are determined using the Gibbs assay:

Gibbs Assay. The cell suspension is adjusted to a constant cell density of 1.00 absorbance unit measured at 600 nm. Then the cells are incubated for exactly one hour at 30°C in the presence of excess dibenzothiophene (DBT) supplied as a saturated ethanol solution. The pH of the culture is then adjusted to 8.0 using a 10% solution of sodium bicarbonate. A $1/100^{\text{th}}$ volume of a 10 mg/mL solution of the Gibbs reagent (2,6-dichloroquinone-4-chloroimide) in ethanol (prepared fresh each day) is added to the cell suspensions, which are further incubated at 30°C for 30 minutes to allow for color development. The cells are then pelleted by centrifugation and the absorbance of the supernatant at 610 nm is measured and used to calculate the concentration of 2-hydroxybiphenyl (2-HBP) present. The desulfurization activity of the cell preparations as measured by the Gibbs assay is multiplied by the volume of the cell preparations used in the biodesulfurization experiments to determine the total amount of biodesulfurization activity. The biodesulfurization activity is expressed as *enzyme units*, where one enzyme unit is the amount of cells required to convert one mmol of DBT to 2-HBP in 1 hour under the standard conditions of the Gibbs assay, or as mg of sulfur that should be removed per hour by the total amount of biocatalyst present in a given experiment. Sulfite is assayed according to the method of Choen and Fridovich, *J. Biol. Chem.* 246:359-366, (1971).

For experiments involving wet cell preparations, *Rhodococcus rhodochrous* IGTS8 cells are grown in defined media according to published procedures,⁹ harvested while in the log phase of growth using centrifugation, and then assayed using the Gibbs assay to determine desulfurization activity. These cells are either used directly in biodesulfurization experiments or are frozen and stored at -70°C until needed.

Biodesulfurization screening experiments are performed by incubating IGTS8 cell preparations with the crude pitch at 30°C and ambient pressure for 16 hours. Because the crude MILDGAS pitch is a solid at room temperature, several methods of providing good contact of the cells with the heavy liquid are to be explored including: (a) freezing the pitch with dry ice and grinding to a fine powder before mixing with an aqueous solution of the freeze-dried cells, and (b) emulsifying the crude pitch with a nonionic surfactant such as Triton N-101 before adding the freeze-dried cells. Typically, one-gram samples of crude

⁹ Kilbane, J.J., and K. Jackowski. 1992. "Biodesulfurization of Water-Soluble Coal-Derived Material by *Rhodococcus Rhodocrous* IGTS8", *Biotechnol. & Bioeng.* 40:1107-1114.

pitch are contacted with 0.1-3.0 grams dry weight of cells. Treated pitch is then recovered from biodesulfurization samples by differential centrifugation in the presence of small amounts of dichloromethane, which is subsequently removed from recovered pitch samples by evaporation.

The results of the screening experiments will determine the feasibility of biodesulfurization of the MILDGAS crude pitch. When the biodesulfurization operating parameters have thus been set, a sufficient quantity of the crude pitch (at least 300 g) will be treated for thermocracking.

Task 3. Flash Thermocracking Screening Tests

The purpose of this task is to obtain sufficient data to enable a comparative technical evaluation of both approaches to producing low-sulfur pitch. The two sulfur-reduced pitches produced in Task 2 are subjected to upgrading to electrode binder pitch specifications using the current FTC reactor. The crude pitch liquid is preheated and pumped cocurrently with a nitrogen stream into the FTC unit where it is rapidly heated to 840°-860°C. Reactor pressure is typically 1.2-1.4 atm.

The FTC unit, shown schematically in Figure 2, consists of a heated sample feed tank, a heated gear pump, an atomizing nozzle, a vertical tubular reactor, a pitch receiver vessel, and a condensing train. A flush tank is also installed to flush the pump and reactor system with solvent following the tests. The atomization of the hot crude pitch with a conventional two-phase spray nozzle requires a carrier gas delivery system. Advanced types of atomizers which do not require large amounts of carrier gas would be available for commercial use, but are beyond the scope of the present program.

The thermal cracker, fabricated from 316 stainless-steel nominal 2-inch Sch40 pipe, is heated by external electrical heaters. A load cell (strain gauge) system is used to monitor and record the weight of the feed material, in order to directly compute the crude pitch feed rate. The carrier/purge gas system sweeps reaction products from the reactor with inert gas. A 50 sL/min mass flow controller maintains a constant carrier gas velocity regardless of transient pressure changes. The atomizing nozzle provides good dispersion of the sample in the form of very small droplets with a controlled particle size distribution. The nozzle is designed to produce a narrow stream of atomized sample droplets in laminar flow, which minimizes contact with the hot walls, thus minimizing coke formation and limiting mesophase particle growth. The resultant binder pitches and pitch cokes are collected for analysis and evaluation. The effluent streams are also analyzed for light oils and gases produced.

Figure 2. SCHEMATIC DIAGRAM OF EXPERIMENTAL PITCH THERMOCRACKING SYSTEM

In a typical test operation, the system is purged with inert gas and the crude pitch is heated to a temperature of adequate fluidity, about 105°C, in the feed tank. The hot pitch is pumped via the heated gear pump into the reactor through the atomizing nozzle or inlet tube assembly, along with the preheated carrier/purge gas. Thermal cracking occurs as the pitch fog moves down the 1.22-m length of the reactor. Pitch coke collects primarily on the reactor walls. A portion of the cracked pitch and some additional coke collects in the receiver, and the remaining pitch, lower-boiling liquids, and water collects in the oil recovery train. A solvent consisting of dichloromethane and tetrahydrofuran (THF) is injected at the oil recovery train inlet to prevent obstruction of the inlet which could be caused by buildup of carryover pitch at the point where the stream temperature drops rapidly.

After cooling the reactor, cracked pitch and coke are removed from the reactor and receiver. Residues are removed from collector surfaces by immersing in liquid nitrogen and scraping or brushing out the embrittled materials. Pitch is then separated from pitch coke by heating to about 90°-120°C to liquefy the pitch and filtering the coke/pitch through a stainless-steel mesh with a pore opening of 103µm.

The condensed solvent/oil/pitch from the condensing train is filtered to recover carryover coke fines. The solvent is removed by rotary vacuum evaporation, the pitch residue is combined with the cracked pitch recovered from the receiver, and the residue is vacuum-distilled to 400°C to yield the finished pitch product. The remaining oils are characterized and stored for later disposal.

It is anticipated that one thermocracking test will be conducted on each of the test liquids. Optionally, a third test may be conducted as a replicate if it is deemed necessary.

Task 4. Test Data Analysis and Interpretation

The data to be analyzed consist of the results of the production of the two reduced-sulfur crude pitches and the FTC screening tests. Yields, operating conditions, and sulfur concentration are the major parameters of interest in the production of the two reduced-sulfur pitches. Screening samples used in biodesulfurization experiments are analyzed for carbon and sulfur by standard ASTM methods. The crude and finished pitches are also analyzed for ring-and-ball softening point, QI, TI, coking value, specific gravity, and elemental composition, plus analyses for mesophase content and carbon forms analysis by transmission microscopy. Other analyses of fuel gases and light oils are performed for the purpose of obtaining yield and material balance data around the thermocracking step. The pitch cokes recovered from the FTC unit are analyzed by proximate and ultimate analyses.

RESULTS AND DISCUSSION

Task 1. Coal Preparation

A 45-kg sample of IBC-109 coal was obtained from the IBCSB. A test screening showed that the coal was about 95% larger than 40 mesh. The coal was therefore crushed and screened twice to obtain a 40×80-mesh (180-425 μ m) fraction, which accounted for 31% of the as-received coal. A total of 5.6 kg of 40×80 coal was thus obtained and stored under nitrogen until used. The oversize (+40 mesh) fraction was set aside for production of starter char in the carbonizer reactor.

Representative samples of +40-mesh, 40×80-mesh, and -80-mesh coal were subjected to proximate and ultimate analyses, and the 40×80-mesh coal was analyzed for sulfur forms. The results of these analyses will be shown in the next quarterly report.

Task 2. Preparation of Coal Liquids

Subtask 2.1. Mild Gasification of IBC-109 Coal

The MBFBR and carbonizer reactors were inspected and prepared for operation. A new electric heating mantle was purchased for the lower section of the MBFBR.

Preparation of starter char in the carbonizer reactor will proceed in the next quarter.

Subtask 2.2. Biodesulfurization of Mild Gasification PRU Crude Pitch

During this quarter, preliminary laboratory-scale experiments were performed to identify means of dispersing/emulsifying crude pitch in water to render it accessible to biocatalysts, and to determine the feasibility of biodesulfurization of this material.

Dispersion of crude pitch in water was attempted by first freezing the pitch at -70°C, cracking it into millimeter-size fragments, and shaking it in water for 24 hours at 30°C. Initially, the particles created a dispersed suspension exposing a relatively high surface area of crude pitch, but almost immediate coalescence was observed and, after an hour of incubation, all of the pitch had coalesced into a few tar balls with correspondingly minimal surface area. Experiments were then performed using surfactants that had previously been shown to be compatible with biodesulfurization catalysts.

Aqueous solutions containing 0.1% of certain non-ionic surfactants had previously been shown to be effective in emulsifying crude oils and unfractionated MILDGAS liquids; however, only minimal emulsification of pitch was obtained under these conditions. Reasonably good dispersion/emulsification of pitch was obtained by heating the pitch, thoroughly blending in surfactants, and then adding the mixture to water, followed by shaking for several hours. A

final surfactant concentration of 0.5% was required in order to achieve reasonable emulsification.

Preliminary biodesulfurization experiments were then performed using two approaches: incubating emulsified crude pitch with biodesulfurization catalysts (concentrated cell preparations) for 16 hours at 30°C, and growing *Rhodococcus rhodochrous* IGTS8 under conditions in which crude pitch is the only source of sulfur. The preferred method of biodesulfurization is to use concentrated biocatalyst preparations and short incubation times, but both approaches were tried to increase the chances that we could quickly determine the feasibility of biodesulfurization of crude pitch.

For experiments employing concentrated cell suspensions, *Rhodococcus rhodochrous* IGTS8 cells were grown in 10L fermenters using BSM medium containing 0.1% glycerol as a carbon source and 1mM DMSO as a sulfur source. After growing to mid-log phase ($OD_{600} = 1.223$), the cells were harvested by centrifugation and added to a shake flask containing one gram of pitch emulsified in BSM using 0.5% diethanolamine surfactant. The total volume of the cell/pitch suspension was 200 mL, which was incubated at 30°C for 16 hours. Then the pitch was recovered by solvent extraction with dichloromethane and submitted for analysis. Sterile controls were also included and submitted for analysis. The desulfurization activity of cell preparation as measured by the Gibbs assay indicated that theoretically the amount of biodesulfurization catalyst present in this experiment could remove as much as 40 mg of sulfur. The sulfur content of the pitch is 2.44% so that one gram contains 24.4 mg sulfur. While the amount of biodesulfurization catalyst included in this experiment then should be capable of completely desulfurizing the pitch, previous experiments employing coal and heavy crude oils have demonstrated that accessibility of the substrate limits the degree of desulfurization. The results of these biodesulfurization tests will be available next quarter.

Experiments were performed to see if IGTS8 could grown in BSM glycerol medium with MILDGAS pitch as the sole source of sulfur. Laboratory-scale shake flask tests demonstrated that IGTS8 could indeed utilize MILDGAS pitch as a sulfur source, but 7 days of incubation at 30°C were required before significant growth was observed. Growth was coincident with dispersion of the pitch, presumably attributable to bioemulsifiers produced by IGTS8. Similar growth tests indicated that IGTS8 does not utilize MILDGAS pitch as a carbon source. Following the successful results obtained in these preliminary growth tests, additional growth tests were performed using one and two gram samples of pitch and in the presence or the absence of 0.1% non-ionic surfactant. Sterile controls were also prepared and processed similarly. After two weeks of incubation at 30°C, the pitch was recovered by centrifugation and extraction with dichloromethane. The samples were submitted for analysis to determine sulfur and carbon values which will be reported next quarter.

During the coming quarter, additional experiments will be performed to define improved methods of obtaining good dispersions/emulsions of MILDGAS pitch that also enable convenient quantitative recovery of pitch. Additionally, bacterial fermentations will be performed to accumulate the large amount of IGTS8 biodesulfurization catalyst needed to treat

the 300g sample of MILDGAS crude pitch required for subsequent thermocracking experiments.

Task 3. Flash Thermocracking Screening Tests

No work was performed on this task during the quarter.

Task 4. Test Data Analysis and Interpretation

Data has been discussed under the Tasks in which the experimental work was performed.

CONCLUSIONS AND RECOMMENDATIONS

At the end of the first quarter, we have shown that IGTS8 can grow with MILDGAS crude pitch as the sole source of sulfur, but does not deplete pitch carbon. An external source of nutrient organic carbon must be provided. IGTS8 cells have been grown which have the biodesulfurization capacity to remove all of the sulfur from one-gram pitch samples, but dispersing the pitch in an aqueous medium to permit sufficient access of the microbes to the pitch surface is the immediate challenge. So far, preliminary results have shown measurable desulfurization when the crude pitch is emulsified through the use of a nonionic surfactant.

In the next quarter, improved dispersion/emulsion of the crude pitch in the biodesulfurization medium will be sought and biodesulfurization screening experiments will be completed. After evaluation of the screening data, the biotreatment of a 300-g crude pitch batch will begin using the selected procedures.

Also next quarter, mild gasification of IBC-109 coal to produce a low-sulfur crude pitch for subsequent flash thermocracking will begin.

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