ABSTRACT

The objective of this program is to investigate the production of electrode binder pitch, valued at $250-$300/ton, from mild gasification liquids. In the IGT MILDGAS process, the 400°C+ distillation residue (crude pitch) comprises up to 20 wt% of maf feed coal. The largest market for pitch made from coal liquids is the aluminum industry, which uses it to make carbon anodes for electrolytic furnaces. In this project, crude MILDGAS pitch is being modified by flash thermocracking to achieve binder pitch specifications.

A 1-kg/h continuous unit has been built for operation up to 900°C at 2.5 atm, and parametric tests were conducted in N₂, H₂ and 50% H₂/N₂. Three key properties (QI, TI, and coking value) appeared to peak around 800°C. The C:H ratio increased while sulfur content decreased with temperature up to 871°C. The softening point peaked around 750°-800°C. Increasing the pitch:gas ratio by 20% further improved the properties. However, addition of H₂ to the reactor gas had adverse effects on QI, TI, and coking value, and failed to reduce sulfur content. In general, thermocracking at 750°-850°C in N₂ resulted in a pitch which meets binder pitch requirements for QI, TI, softening point, and C:H ratio. Further improvements in density and sulfur content are required.

Test anodes were prepared by Alcoa using the upgraded mild gasification pitch. All of the key anode properties (density, strength, resistivity, thermal properties, permeability, and reactivity) compared very favorably with those of electrodes made from a standard pitch binder.

A first-cut process flow diagram based on the test data has been developed. Future work will address methods of reducing pitch sulfur content and utilizing pitch coke.
EXECUTIVE SUMMARY

The objective of this program is to investigate the production of electrode binder pitch from mild gasification liquids. The IGTLIDGAS 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, not much work was done in the past to improve the properties of low-temperature pitches, primarily because there is no longer a low-temperature carbonization industry in most industrialized nations where aluminum smelters operate. 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.

Some of the important pitch properties and their desired ranges are: quinoline insoluble (QI) content (8-12%), toluene insoluble (TI) content (26-32%), softening point (88-121°C), coking value (55-60%), density (≥1.32 g/cm³), C:H ratio (≥1.75), and sulfur (≤0.6%). A distinction between "primary" and "secondary" QI is also important. Primary QI is formed prior to pitch condensation in the coke oven, while larger-diameter secondary QI can be generated by
slow heat treatment of a QI-lean pitch. It is likely that the more desirable primary QI is formed by polycondensation reactions of pitch components in vapor or aerosol droplet form, which limits the growth of mesophase spherules.

The process under study in this project is predicated on the benefits of rapid heating of atomized pitch -- flash thermocracking -- to achieve desirable pitch properties. By use of a flash thermocracker (FTC), primary QI can be formed simultaneously with dealkylation, dehydration, and aromatization reactions and removal of lower-boiling components from a mild gasification pitch. The results of a previous (1963-1973) U.S. Bureau of Mines study on the upgrading and utilization of low-temperature lignite tars form the foundation for the current experimental work.

In this project, the upgrading of a crude pitch fraction from the DOE-sponsored MILDGAS process research unit (PRU) program is being studied. The test material was obtained from PRU tests with Illinois No. 6 coal in April-May, 1990. In the first year of the current project, a FTC unit was constructed to operate at temperatures of 650°-900°C under low-pressure inert or reducing gas. Thermocracking tests were performed in N₂ at temperatures of 650°-815°C, and analyses showed significant improvements in properties.

In the current 12-month program, additional tests were conducted to determine the effects of higher temperature (815°-870°C), crude pitch:gas ratio (0.91-1.12×10⁴), and a reducing atmosphere (50-100% H₂) on product yield and quality. The thermocracker was first fitted with several improvements, including a 32-point datalogger to monitor and record temperatures, pressures, and flows; an electronic load cell; a larger-capacity primary product receiver with a coalescing outlet filter; pressure transducers on the pitch inlet line and the gas outlet from the primary product receiver; and a larger dry ice cooler/coalescing column and 5-L condensate collector. With these improvements, five parametric tests were performed on the same MILDGAS PRU crude pitch used in previous tests. The results of these tests are summarized as follows.

Temperature Effects: when the peak thermocracker temperature was increased from 650°C to 871°C, the thermocracker yields in N₂ were affected as follows: finished pitch decreased from 54.4% to 28.7%, pitch coke increased from 13.0% to 27.9%, oils decreased from 27.8% to 8.2%, and gas increased from 2.9% to 35.0%. The water yield ranged 0.2% to 2% without a clear trend.
Compared to the crude (raw) MILDGAS pitch:

- QI increased from 0.01% to 13.6% at 815°C, TI from 7.0% to 33% at 760°C, and caking value from 24.0% to 50.3% at 760°C.
- C:H ratio increased from 0.99 to 1.64, and sulfur content decreased from 2.44% to 2.01% over the entire test temperature range up to 871°C.
- Pitch density increased from 1.16 to about 1.21 g/cm³ with increasing temperature.
- Softening point increased from 40°C to 113°C at a thermocracker temperature of 760°C, but then decreased with temperature to about 83°C at a thermocracker peak temperature of 871°C.

Reducing Gas Effects: when the carrier gas was changed from 100% N₂ to 100% H₂, the thermocracker yields at 870°C were affected as follows: finished pitch decreased from 28.7% to 18.8%, pitch coke decreased from 27.9% to 15.1%, oils increased from 8.2% to 16.1%, and gas increased from 35.0% to 45.9%. The water yield increased slightly from 1-2% to about 2.7%.

Compared to thermocracking under N₂, H₂ had these effects on pitch quality:

- QI decreased from 8.7% to 2.1%, TI decreased from 27.2% to 18.2%, and caking value decreased from 46.8% to 42.8%
- C:H ratio decreased from 1.64 to 1.56, while sulfur content remained essentially unchanged at 2.0%-2.1%
- Pitch density increased slightly from 1.21 to 1.26 g/cm³.
- Softening point decreased from 83°C to 71°C.

In general, the addition of H₂ to the thermocracker atmosphere had deleterious effects on pitch yield and all of the quality criteria except density, and did not significantly reduce the sulfur content. Therefore, no further work was done using H₂ as a component of the thermocracker carrier gas.

Pitch:Gas Ratio Effects: For thermocracking under N₂ at 871°C, increasing the pitch:gas volumetric ratio from 0.91×10⁻⁴ to 1.10×10⁻⁴ caused a moderate decrease in pitch (24.8%) and gas (29.0%) yields with increased pitch coke (32.4%) and oil (12.0%) yields. However, the pitch quality generally improved:

- QI increased from 8.7% to 13.4%, TI from 27.2% to 29.4%, and coking value from 46.8% to 50.1%.
- C:H ratio increased from 1.64 to 1.75, while sulfur remained unchanged at 2.0%.
- Pitch density decreased slightly from 1.21 to 1.18 g/cm³.
- Softening point increased from 83°C to 104°C.

With the exception of sulfur, all of the finished pitch properties resulting from thermocracking under N₂ at 855°-871°C are within or nearly within the ranges specified for a typical binder pitch. These conditions were selected for preparation of a 0.7-kg sample of finished pitch from the MILDGAS crude pitch, which was then used as a binder to prepare test anodes.

The test anodes were prepared by Alcoa, using a conventional petroleum coke filler, and characterized for critical properties. When compared with anodes made from premium conventional pitch at similar binder:filler weight ratios (0.22-0.25), the test anodes showed very similar properties. The baked density (1.49-1.52 g/cc), resistivity (61.8-62.4 μohm·m), thermal conductivity (2.5-2.9 W/m-K), flexural strength (6.4-12.1 MPa), compressive strength (44-43 MPa), Young's modulus (3 GPa), air permeability (1.64-2.67 nPm), CO₂ reactivity (4.2-4.5 wt% loss), and air reactivity (19.2-21.5 wt% loss) were equal to or better than the standard electrodes. The thermal expansion was slightly higher in the IGT anodes (4.1-4.4x10⁻⁶/K) than in the standard anodes (3.8-4.1x10⁻⁶/K), but the difference was less than 8%, which was not statistically significant.

A mass-balanced block flow diagram for production of mild gasification pitch was prepared, and showed that about 99 lb of finished pitch, 101 lb of green pitch coke, and 39 lb of high-BTX oil could be produced for each maf ton of Illinois No. 6 feed coal. It is estimated that the value of these products could offset the entire cost of the feed coal, leaving the major mild gasification products -- form coke and chemical feedstocks -- unburdened of the coal cost.

Future continuation of this research will address the problem of reducing the pitch sulfur content, develop the potential for pitch coke, and update the process flow diagram to include the best available data.
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. This includes determination of the operating conditions of temperature, crude pitch feed rate, gas atmosphere, and atomization of the crude pitch that yield a suitable specification-grade electrode binder pitch. Treated pitch samples are to be evaluated in terms of density, softening point, coking value, quinoline insolubles (QI), toluene insolubles (TI), mesophase content, ash, and elemental analysis. Material balances will be obtained to determine the yields of cracked pitch, pitch coke, gases, and oils.

The task structure of the current year is as follows:

Task 1. Sample Preparation
Task 2. Equipment Construction and Shakedown
Task 3. Pitch Thermocracking Tests
Task 4. Electrode Preparation and Testing
Task 5. Product Characterization and Testing
Task 6. Data Analysis and Interpretation
Task 7. Process Scale-Up Design
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. 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.

However, 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.\(^1\) \(^2\) \(^3\) \(^4\) 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. Currently, to fulfill this need, the MILDGAS design calls for the addition of a thermal cracker to the hot effluent gas stream from the gasifier. However, if the thermal treatment is performed on the condensed liquids rather than on the entire effluent stream, the amount of material handled will be reduced by over 50%. This will reduce the heat load for the thermal cracker, lowering capital and operating costs of the process.

Some of the tar and/or pitch properties that most influence electrode performance are:

- Quinoline insoluble (QI) content -- this portion of the pitch has an important role in achieving the desired grain structure in the electrodes. There is also an


important distinction between "primary" and "secondary" QI, also designated $\alpha_1$- and $\alpha_2$-resins. Primary QI ($\alpha_1$) consists of insoluble soot-like particles of 10-100$\mu$m diameter in the original tar. A level of 8-12 wt% primary QI in the pitch is considered desirable. Secondary QI ($\alpha_2$) comes from heating the molten pitch to promote further cracking/condensation, forming spherical "mesophase" particles. Excessive amounts of coalesced mesophase adversely affects the rheology and wetting properties of the pitch. Mesophase should comprise no more than about 10% of the total QI, and the primary QI should be predominantly smaller than 4$\mu$m in diameter.

- Toluene insoluble (TI) content -- this portion of pitch, like QI, is an indicator of the degree of polycondensation, and is generally regarded as being in correlation with key physicochemical properties. A TI value of 26-34% is typical for a specification anode pitch. TI which are quinoline-soluble are also designated as $\beta$-resins.\(^5\)

- Softening point -- this is a measure of viscosity development in heated pitch. A good electrode binder pitch should have a softening point (ring-and-ball) of 88°C or higher.

- Coking value -- this is the yield of solid coke upon carbonization. The coking value for a good binder pitch should be 55% or higher.

Pitch consumers will reject a pitch that has excessive secondary QI. It is likely that the more desirable primary QI is formed by polycondensation reactions of pitch components in vapor or aerosol droplet form, which dimensionally limits the growth of mesophase spherules. By achieving rapid heating of small droplets of pitch in an FTC, primary QI can be formed simultaneously with dealkylation, dehydration, and aromatization reactions and removal of lower-boiling components from the pitch. The results of a previous U.S. Bureau of Mines study on the upgrading and utilization of low-temperature lignite tars.

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over 1963-73 support this conclusion, and form the foundation for the proposed experimental work.\textsuperscript{6,7,8,9}

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. One of the major concerns is the sulfur content of the pitch, which naturally results from the processing of high-sulfur coals. Users of coal tar pitch for electrode binders generally require a sulfur content no higher than 0.6 \text{wt}\%, which is typical of a conventionally derived pitch from Eastern coking coals. In this project, IGT is exploring one possible method of reducing the sulfur content of the pitch --- introducing H\textsubscript{2} to the thermocracker --- while continuing to improve its properties. A study of coal hydropyrolysis\textsuperscript{10} has shown that mild hydrocracking can actually increase the aromaticity of pyrolysis liquids by reacting preferentially with aliphatic groups. Therefore, the reaction of H\textsubscript{2} with organically-bound sulfur in the pitch may take place at low to moderate pressures without adding significant hydrogen to the pitch, and may actually improve the aromaticity of the product.

The current project aims to: investigate the effects of rapid thermal cracking of atomized MILDGAS crude pitch; 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.

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EXPERIMENTAL PROCEDURES

Task 1. Sample Preparation

The mild gasification test liquid (crude pitch) to be used in this project was produced in the IGT MILDGAS process research unit (PRU), during a previous U.S. DOE project, in April-May, 1990. 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 500°F (260°C). The resultant crude pitch is a solid at room temperature.

The materials from three MILDGAS tests (IST-5, IST-7, and IST-9) were combined to yield a 20-lb composite sample. These three PRU tests were all operated at nearly identical conditions of 1110±5°F (599±3°C), 10 psig (0.17 MPa), 11±2 min solids residence time, in a 100% N₂ fluidizing atmosphere. The feedstock was a 1:1 (w/w) mixture of Illinois No. 6 coal and recycled char from previous PRU tests.

Because of the availability of the MILDGAS crude pitch from the PRU, IBCSF coal samples are not being used in this program. The coal used to produce the test samples was an Illinois No. 6 coal similar to IBC-101.

The composite test liquid are to be characterized according to the methods outlined in Task 5 to evaluate any changes that have taken place during storage.

Task 2. Equipment Construction and Shakedown

The pitch thermocracking test unit 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. The carrier/purge gas system sweeps reaction products from the reactor with inert gas. 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. In tests without atomization, the atomizing nozzle assembly is replaced an inlet assembly consisting of coaxial 1/4-inch and 1/2-inch 316SS tubes.

Several minor but important improvements are to be installed in the current program:

- A high-capacity (50 sL/min) mass flow controller to maintain a constant carrier gas velocity regardless of transient pressure changes,
- A pressure transducer to monitor the pitch pressure between the pump and nozzle
- A pressure transducer to monitor reactor outlet pressure, and
- A load cell (strain gauge) system to monitor and record the weight of the feed material, in order to directly compute the crude pitch feed rate.

A simplified schematic diagram of the thermocracker test unit, including the improvements installed during the current project year, is shown in Figure 1.

Task 3. Pitch Thermocracking Tests

Approximately 12 thermocracking tests are planned to examine the effects of thermocracking temperature, pitch residence time, gas atmosphere, and pitch: gas volumetric ratio on product quality and yield. Tests may also be performed with and without the use of the atomizing nozzle to confirm its effectiveness in promoting more thorough cracking of the pitch and production of primary QI, and also in controlling the amount of coke formation. Gas atmospheres to be used include N₂, 50% H₂:N₂, and 100% H₂. All tests will be conducted at minimum sustainable pressure up to a maximum of 20 psig (0.24 MPa).
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 48-inch (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 103 μm.

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 with the filtered coke fines, 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.

Task 4. Electrode Preparation and Testing

The most direct method of evaluating potential performance of a binder pitch is the fabrication and evaluation of test electrodes. First, the filler is preheated for 12 h at 200°C, then blended with the binder pitch in an oil-heated sigma-blade mixer at 60°C above the pitch softening point. The hot paste is then transferred to an oil-heated floating mold press and pressed at 600 atm to produce 5-cm-diameter × 12-cm-long cores. The cores are cooled to room temperature and then baked in an electric furnace packed in fluid coke. The baking schedule is: 20-150°C at 100°C/h, 150-300°C at 10°C/h, 300-1100°C at 50°C/h, and soak at 1100°C for 20 h. The test batch is then slowly cooled to room temperature and the cores are subjected to physical, electrical, and chemical tests.

The pitch product with the most suitable characteristics is selected for electrode fabrication. Electrodes are produced from the selected pitch and conventional petroleum coke which is provided by Alcoa. Control anodes are also produced using a conventional premium coal tar pitch binder. A series of four blends with 14%, 16%, 18%, and 20% by weight of pitch are prepared using the conventional pitch supplied by Alcoa, and two preferred binder:filler ratios are selected. With the IGT pitch, two blends are then prepared using these selected volumetric binder:filler ratios, corrected for differences in the measured densities of the two pitches. Two test anodes are cored from each blend with the Alcoa pitch, and three from each blend with IGT pitch, and these anodes are subjected to the test series described below.
Task 5. Product Characterization and Testing

The crude and cracked pitches are characterized at IGT by means of the following analyses:

- Quinoline insolubles (ASTM D2318)
- Toluene insolubles (ASTM D4312)
- Softening point, Ring-and-Ball (ASTM D97)
- Coking value (modified ASTM D2416)
- Elemental composition (modified ASTM D3178)
- Specific gravity (ASTM D70)

Proximate and ultimate analyses of "green" (e.g., not calcined) pitch coke are to be performed for all successful tests.

Test electrodes prepared in Task 4 are subjected to a series of tests and analyses, including:

- Real and baked apparent density
- Resistivity
- Flexural strength
- Compression strength
- Young's modulus
- Coefficient of thermal expansion (CTE)
- Thermal conductivity (TC)
- Air permeability
- CO$_2$ reactivity
- Air reactivity
- Elemental analysis (including Al, Ba, Ca, Cl, F, Fe, K, Mg, Na, Ni, P, Pb, Si, Ti, S, and V)

The anode tests are performed by Alcoa at their laboratory in Badin, North Carolina.

Task 6. Data Analysis and Interpretation

The primary goal of these experiments is to build a database on thermocracking of mild gasification pitch made from
Illinois No. 6 coal that can be used as a basis for process design and scale-up.

The principal data relevant to the project objectives are:

- Material balance data for conversion of crude pitch to binder-quality pitch, pitch coke, by-product oils, water, and fuel gas
- Increases in softening point, density, primary QI, TI, coking value, and C/H atomic ratio without excessive development of mesophase
- Decreases in heteroatom (N, S, and O) content
- Physical and electrical properties of test electrodes made from the thermally cracked pitch product, aimed at maximizing density, strength, and thermal conductivity, and minimizing resistivity, CTE, permeability, and reactivity.

The thermocracking data are presented in terms of: pitch conversion as a function of thermocracker temperature, pitch:gas volumetric ratio, pitch residence time, and percent $H_2$ in carrier gas; and percent approach to each key property specification as determined by test data on a commercial pitch sample.

The electrode test data are presented in terms of each physical, chemical, and electrical property in comparison with the properties of the anodes (controls) prepared with conventional binder.

Task 7. Process Scale-Up Design

The test data, especially material balances, are used as a basis for a block flow design of flash thermocracking for mild gasification pitch. The current mild gasification PDU design developed in an ongoing DOE/METC-sponsored program is used as a backdrop for a conceptual integrated pitch cracking operation. The preferred process conditions to obtain specification-grade binder pitch and/or pitch coke dictate the material balances, which are then used to produce a block flow diagram of the process integrated with mild gasification. The implications of the design for demonstration and commercial-scale plant design are also discussed.
RESULTS AND DISCUSSION

Task 1. Sample Preparation

The crude pitch sample remaining from the previous year was analyzed, and no significant changes were observed in the pitch characteristics. The crude pitch was thoroughly mixed before charging to the feed reservoir.

Task 2. Equipment Construction and Shakedown

The planned improvements to the thermocracker were completed during the first two quarters. Based on operating experiences during the project, four additional changes were also made:

- A larger-diameter pitch receiver which eliminated a restriction due to a pipe size reduction was installed. This was done to avoid a buildup of pitch coke at the reactor exit which had previously caused fluctuations in gas flow and reactor pressure.

- A 5-micron strainer was installed on the recycle line from the pitch pump back to the reservoir, to remove any solids which could obstruct pitch flow through the atomizing nozzle, and an extended pre-test recycle period was included in the test procedure.

- A high-capacity Pyrex cooling/coalescing tower filled with Raschig-ring packing was installed in place of three smaller vessels, in order to improve pitch collection from the gas stream and facilitate cleanup.

- A coalescing filter was later installed inside the pitch receiver vessel upstream of the gas outlet. This was done to prevent buildup of pitch in the receiver exit line, allowing longer test durations.

Task 3. Pitch Thermocracking Tests

Six parametric thermocracking tests were conducted during the year, five of which yielded acceptable data. Table 1 below shows the conditions of these tests.

Test 1-021894 was completed successfully, but a minor laboratory accident resulted in the destruction of a portion of the sample, and so no usable data was produced. The samples from the remaining five tests were fully characterized, and the data are shown and discussed under
Table 1. PARAMETRIC THERMOCRACKING TEST CONDITIONS

<table>
<thead>
<tr>
<th>Test #</th>
<th>Reactor Temps, °C (Upper/Lower)</th>
<th>Gas Pres, atm</th>
<th>Carrier Gas</th>
<th>Residence time, s</th>
<th>Pitch:Gas Vol Ratio (x10^-4)</th>
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<tr>
<td>1-021894</td>
<td>846/872</td>
<td>1.31</td>
<td>100% N₂</td>
<td>2.06</td>
<td>0.98</td>
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<tr>
<td>2-033194</td>
<td>842/873</td>
<td>1.14</td>
<td>50% H₂/N₂</td>
<td>2.10</td>
<td>1.01</td>
</tr>
<tr>
<td>3-040594</td>
<td>832/871</td>
<td>1.03</td>
<td>100% H₂</td>
<td>1.86</td>
<td>0.90</td>
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<td>1.32</td>
<td>100% N₂</td>
<td>2.42</td>
<td>0.91</td>
</tr>
<tr>
<td>4-041894</td>
<td>785/816</td>
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<td>2.38</td>
<td>1.06</td>
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<td>7-042294</td>
<td>841/871</td>
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<td>100% N₂</td>
<td>2.22</td>
<td>1.10</td>
</tr>
</tbody>
</table>

Product Characterization and Testing and Data Analysis and Interpretation.

Test 2-033194 was conducted to investigate the effects of introducing H₂ into the carrier gas. A total of 153g of crude pitch were fed at an average rate of 8.6 g/min. The test was interrupted twice when the pitch nozzle pressure rose sharply, indicating an obstruction in the nozzle. After each interruption, the reactor was raised about 2.5 cm to decrease the temperature at the nozzle tip. Decreasing this temperature from 450°C to about 320°C eliminated the problem of nozzle plugging, and the test was completed.

Test 3-040594 was conducted to determine the effects of thermocracking in pure H₂ at conditions similar to the previous test. A total of 259g of crude pitch were fed at 8.6 g/min. Operationally, a notable difference in this test was the low exit gas pressure of 0.105 MPa, compared to a typical pressure of 0.13-0.14 MPa in other tests at similar flow rates. The reason for this effect is uncertain, but may be related to the low-temperature properties of the product pitch accumulating in the cold trap and mist filters.

Test 4-041894 was performed to compare the use of 50% H₂ in the carrier gas at lower reactor temperatures. This test can be directly compared with Test 2-033194. 317g of crude pitch were fed at about 7.9 g/min.

Test 7-042294 was conducted to determine the effects of a higher pitch:gas loading in inert gas. This test can be compared to Test 1-041194, which used lower pitch and gas rates. A total of 358g of crude pitch were fed at an average feed rate of 8.8 g/min. One of the operational similarities noted in this test and the previous test under N₂ is a gradual buildup of pitch nozzle pressure, which did not occur in the tests with H₂ in the carrier gas. This
suggests that H₂ inhibits the buildup of condensed or coked material around the nozzle tip.

Task 4. Electrode Preparation and Testing

A series of production runs were performed at a single set of conditions to produce enough finished pitch for electrode preparation. This series consisted of 11 segments each feeding up to 584 g of crude pitch. The nominal conditions selected for these runs were: 840°C (upper section), 870°C (lower section), carrier gas 100% N₂, residence time 2.5 s, pitch:gas volumetric ratio 1.1x10⁻⁴.

The conditions used in the pitch production runs for electrode fabrication are shown in Table 2 below.

### Table 2. THERMOCRACKING CONDITIONS FOR ELECTRODE PRODUCTION

<table>
<thead>
<tr>
<th>Run #</th>
<th>Crude Pitch fed, g</th>
<th>Reactor Temp, °C (Upper/Lower)</th>
<th>Gas Pres, atm</th>
<th>Carrier Gas</th>
<th>Res time, s</th>
<th>Pitch:Gas Vol Ratio (x10⁻⁴)</th>
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</thead>
<tbody>
<tr>
<td>5-052794A</td>
<td>75</td>
<td>841/893</td>
<td>1.03</td>
<td>100% N₂</td>
<td>2.05</td>
<td>1.26</td>
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<tr>
<td>5-060194B</td>
<td>60</td>
<td>835/891</td>
<td>1.17</td>
<td>&quot;</td>
<td>2.12</td>
<td>0.89</td>
</tr>
<tr>
<td>5-060294C</td>
<td>572</td>
<td>841/871</td>
<td>1.44</td>
<td>&quot;</td>
<td>2.63</td>
<td>1.25</td>
</tr>
<tr>
<td>5-060794D</td>
<td>558</td>
<td>841/868</td>
<td>1.31</td>
<td>&quot;</td>
<td>2.62</td>
<td>1.18</td>
</tr>
<tr>
<td>5-061094E</td>
<td>584</td>
<td>841/866</td>
<td>1.34</td>
<td>&quot;</td>
<td>2.69</td>
<td>1.18</td>
</tr>
<tr>
<td>5-062294F</td>
<td>390</td>
<td>832/866</td>
<td>1.31</td>
<td>&quot;</td>
<td>2.93</td>
<td>1.10</td>
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<tr>
<td>5-062794G</td>
<td>501</td>
<td>838/866</td>
<td>1.34</td>
<td>&quot;</td>
<td>2.69</td>
<td>0.85</td>
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<tr>
<td>5-062894H</td>
<td>68</td>
<td>838/871</td>
<td>1.34</td>
<td>&quot;</td>
<td>2.56</td>
<td>0.43</td>
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<tr>
<td>5-071994I</td>
<td>512</td>
<td>832/860</td>
<td>1.27</td>
<td>&quot;</td>
<td>2.86</td>
<td>1.33</td>
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<td>5-072094J</td>
<td>130</td>
<td>832/866</td>
<td>1.27</td>
<td>&quot;</td>
<td>2.44</td>
<td>1.07</td>
</tr>
<tr>
<td>5-072094K</td>
<td>249</td>
<td>832/866</td>
<td>1.34</td>
<td>&quot;</td>
<td>2.57</td>
<td>0.92</td>
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</table>

The first two runs were stopped early because of plugging at the pitch receiver outlet. The outlet size was increased from 3/8" to 1/2" and Run 5-060294C was performed. Following that run, a coalescing filter was installed inside the pitch receiver to prevent buildup of pitch in the exit line. This was found to permit easier cleanup and recovery of neat pitch, because the pitch fog coalesced inside the filter cavity and drained back down into the receiver. Eventually, however, the pressure drop across the filter increased to the point the run had to be ended. This configuration was used for the remaining production runs. A total of 3699 g of crude pitch was fed, from which a total of 718 g of finished pitch was recovered for testing. An
additional 100-200 g of unrecovered product pitch was discarded with used filter elements.

Finished pitch was recovered from each of these runs by the established method described in EXPERIMENTAL PROCEDURES, and all of the recovered samples were then combined into a single batch. This batch was delivered to an Alcoa laboratory in Badin, North Carolina for conversion into electrodes by the method previously described.

Prior to preparation of the IGT-based anodes, a series of control anodes was prepared by Alcoa, using a conventional coal tar pitch with a similar softening point. These anodes were prepared with blends of 14 wt%, 16 wt%, 18 wt%, and 20 wt% of binder. The filler was a conventional petroleum coke used at Alcoa for production of prebaked anodes. These anodes were then cored in duplicate, and the cores were characterized for density, resistivity, thermal expansion, thermal conductivity, flexural and compressive strength, Young's modulus, air permeability, CO₂ reactivity, and air reactivity. From these data, it was concluded that the best properties were obtained in the anodes made from 18-20 wt% pitch. Anodes were then prepared from the IGT pitch, using the same petroleum coke filler, at volumetric ratios corresponding to 19 wt% and 21 wt% of the conventional pitch. Because of the density differences between the pitches, the corresponding weight percentages for the IGT-based mixes were 18.2 wt% and 20.1 wt% pitch.

Task 5. Product Characterization and Testing

The product characterization data from pitch thermocracking tests performed this year, including the composite of the production runs for test electrode pitch, are shown in Table 3. The test data in Table 3 are listed in order of test matrix designations rather than chronologically.

The anode test data from Alcoa are shown in Table 4. Data from the anodes made with conventional binder and with the MILDGAS-derived pitch binder, each at the 18% and 20%-binder levels, are included. Note that the real density and chemical analysis were not performed on the control anodes, but that ranges of typical values for the chemical analysis of conventional anodes are given.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Typical Electrode Pitch</th>
<th>Crude MILDGAS Pitch</th>
<th>Test 1-041194</th>
<th>Test 2-033194</th>
<th>Test 3-040594</th>
<th>Test 4-041894</th>
<th>Test 5-5A-K (anodes)</th>
<th>Test 7-042294</th>
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<tbody>
<tr>
<td>Test Temp (Upper), °C</td>
<td>--</td>
<td>--</td>
<td>841</td>
<td>842</td>
<td>832</td>
<td>785</td>
<td>837</td>
<td>841</td>
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<tr>
<td>Test Temp (Lower), °C</td>
<td>--</td>
<td>--</td>
<td>869</td>
<td>873</td>
<td>871</td>
<td>816</td>
<td>869</td>
<td>871</td>
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<td>Residence Time, s</td>
<td>--</td>
<td>--</td>
<td>2.42</td>
<td>2.10</td>
<td>1.86</td>
<td>2.38</td>
<td>2.68</td>
<td>2.22</td>
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<tr>
<td>Pitch:Gas Vol Ratio (×10³)</td>
<td>--</td>
<td>--</td>
<td>0.91</td>
<td>1.01</td>
<td>0.90</td>
<td>1.06</td>
<td>1.12</td>
<td>1.10</td>
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<td>Carrier Gas</td>
<td>--</td>
<td>--</td>
<td>100% N₂</td>
<td>50% H₂</td>
<td>100% H₂</td>
<td>50% H₂</td>
<td>100% N₂</td>
<td>100% N₂</td>
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**YIELDS**

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<td>--</td>
<td>27.87</td>
<td>27.17</td>
<td>18.83</td>
<td>27.23</td>
<td>20.67</td>
<td>25.20</td>
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<td>--</td>
<td>27.01</td>
<td>15.06</td>
<td>16.17</td>
<td>18.32</td>
<td>23.88</td>
<td>32.94</td>
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<td>15.15</td>
<td>16.30</td>
<td>12.55</td>
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<td>36.69</td>
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<td>1.28</td>
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<td>1.78</td>
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**PITCH PROPERTIES**

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<td>2.1</td>
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<td>13.4</td>
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<td>23.2</td>
<td>18.2</td>
<td>20.6</td>
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<td>29.4</td>
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<td>Softening Pt (R&amp;B), °C</td>
<td>88-121</td>
<td>40</td>
<td>83</td>
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<td>71</td>
<td>93</td>
<td>84</td>
<td>104</td>
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<td>1.23</td>
<td>1.26</td>
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<tr>
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<td>1.97</td>
<td>2.05</td>
<td>2.27</td>
<td>2.12</td>
<td>2.07</td>
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<tr>
<td>Oxygen (by diff)</td>
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<td>1.34</td>
<td>2.98</td>
<td>1.15</td>
<td>2.78</td>
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<tr>
<td>C:H Atomic Ratio</td>
<td>1.75</td>
<td>0.99</td>
<td>1.64</td>
<td>1.65</td>
<td>1.56</td>
<td>1.52</td>
<td>1.56</td>
<td>1.75</td>
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**PITCH COKE PROPERTIES, wt% maf**

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<tbody>
<tr>
<td>Carbon</td>
<td>--</td>
<td>--</td>
<td>89.58</td>
<td>89.66</td>
<td>91.30</td>
<td>90.19</td>
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<td>Hydrogen</td>
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<td>3.30</td>
<td>3.05</td>
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<td>3.18</td>
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<td>2.90</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>--</td>
<td>--</td>
<td>1.33</td>
<td>1.39</td>
<td>1.43</td>
<td>1.35</td>
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<tr>
<td>Sulfur</td>
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<td>--</td>
<td>1.93</td>
<td>1.79</td>
<td>1.82</td>
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<td>Oxygen (by diff)</td>
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<td>3.97</td>
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<td>Anode density, g/cm³</td>
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<td>1.502</td>
<td>1.503</td>
<td>1.499</td>
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<td>Resistivity, μΩcm·m</td>
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<td>69.0</td>
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<td>Air permeability, nPm</td>
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<td>CO₂ reactivity, wt% loss</td>
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Chemical analysis, ppm

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<td>1.82</td>
<td>--</td>
</tr>
<tr>
<td>Vanadium</td>
<td>80 - 260</td>
<td>--</td>
<td>111</td>
<td>--</td>
</tr>
</tbody>
</table>

* Typical values
Task 6. Data Analysis and Interpretation

The data in Table 3 show the effects of thermocracker temperature, carrier gas composition, and pitch:gas loading on product yields and on pitch properties. The observations based on the data can be summarized as follows:

**Effects of Thermocracker Temperature**

The examination of data from tests performed this year and last year under N₂ at roughly comparable residence times and pitch:gas loading show that the thermocracker yields were affected by increasing peak thermocracker temperature (pitch:gas vol ratio of 0.9×10⁻⁴) from 650°C to 871°C as follows:

- Finished pitch decreased from 54.4% to 28.7%
- Pitch coke increased from 13.0% to 27.9%
- Oils decreased from 27.8% to 8.2%
- Gas increased from 2.9% to 35.0%
- Water yield ranged 0.2% to 2% without a clear trend.

The yield data as a function of thermocracker temperature are displayed graphically in Figure 2.

![Figure 2. EFFECT OF TEMPERATURE ON THERMOCRACKER YIELDS](image-url)
Pitch quality criteria were also affected significantly by reactor temperature. Compared to the crude (raw) MILDGAS pitch:

- QI increased from 0.01% to about 13.6% at 815°C, TI from 7.0% to about 33% at 760°C, and coking value from 24.0% to 50.3% at 760°C. These data are shown in Figure 3.

![Figure 3. EFFECT OF TEMPERATURE ON QI, TI, AND COKING VALUE](image)

- C:H ratio increased from 0.99 to 1.64, and sulfur content decreased from 2.44% to 2.01% over the entire test temperature range up to 871°C. These data are shown in Figure 4.
- Pitch density increased from 1.16 to about 1.21 g/cm³ with increasing temperature. These data are also shown in Figure 4.
- Softening point increased from 40°C to 113°C at a thermocracker temperature of 760°C, but then decreased with temperature to about 83°C at a thermocracker peak temperature of 871°C. These data are also shown in Figure 4.
Effects of Hydrogen in Thermocracker

H₂ in the carrier gas decreased the pitch coke formation and increased gas, light oil, and water yields, indicating significant hydrocracking activity. Under 50 vol% H₂/N₂ the pitch yield was not significantly affected, but by switching the carrier gas from 100% N₂ to 100% H₂ the pitch yield decreased from 28.7% to 18.8%, pitch coke decreased from 27.9% to 15.2%, oils increased from 8.2% to 16.1%, and gas increased from 35.0% to 45.9%. The water yield increased slightly from 1-2% to about 2.7%. The effects of H₂ in the carrier gas on yields are plotted in Figure 5.

The use of H₂ in the carrier gas did not reduce the sulfur content of the finished pitch as we had predicted. However, the effects of H₂ on other pitch properties was significant. The QI and TI content decreased at both levels of H₂ content. In 100% H₂, QI decreased from 8.7% to 2.1%, TI decreased from 27.2% to 18.2%, and coking value decreased from 46.8% to 42.8%, compared to pitch produced in N₂.
Figure 5. EFFECT OF CARRIER GAS HYDROGEN ON THERMOCRACKER YIELDS

The effects on coking value, softening point, and pitch density under 50 vol% H$_2$ were somewhat ambiguous, but pitch produced under pure H$_2$ was definitely affected adversely, showing decreased coking value and softening point as well as low QI and TI values. Compared to pitch produced under N$_2$, 100% H$_2$ had the following effects: C:H ratio decreased from 1.64 to 1.56, while sulfur content remained essentially unchanged at 2.0%-2.1%; pitch density increased slightly from 1.21 to 1.26 g/cm$^3$; and softening point decreased from 83°C to 71°C.

The effects of H$_2$ on QI, TI, and coking value are shown in Figure 6, and the effects of H$_2$ on specific gravity, softening point, C:H ratio, and sulfur are shown in Figure 7.

From these data, we must conclude that conducting the flash thermocracking under a H$_2$-rich atmosphere does not appear to confer any benefits on the pitch upgrading process, at least for purposes of producing an acceptable electrode binder pitch.

Effects of Thermocracker Pitch Loading

In Test 7-042294, the conditions of temperature and gas atmosphere (100% N$_2$) were similar to those in Test 1-041194, but the former test operated at a 9% shorter residence time and a 21% higher pitch loading (pitch:gas volumetric ratio).
The difference in residence times was probably not significant, so changes observed in yield and product quality can be attributed to the difference in pitch loading. The yields were slightly affected, with the higher pitch loading resulting in 10% less cracked pitch, 22% more pitch coke, and 13% less gas. Figure 8 shows the effects of pitch loading on thermocracker yields in these two tests.
The pitch properties were significantly better at the higher pitch rate, with QI (13.4 wt%), TI (29.4 wt%), and softening point (104°C) falling in the ranges for typical electrode pitch. The coking value (50.1 wt%) was slightly below the desired range of 55-60 wt%. The specific gravity (1.18) was lower than expected, but the C:H ratio of 1.75 was the highest produced to date, equaling that of a specification binder pitch. Sulfur in the finished pitch remained unchanged at about 2.0 wt%. Figures 9 and 10 show the influence of this operating parameter on the key pitch properties.

Because of these results, the conditions of Test 7-042294 were selected as nominal operating conditions for preparing the larger batch of pitch for electrode preparation.

Test Electrodes

Test anodes were made successfully from the MILDGAS-based pitch, using 18 wt% and 20 wt% of binder and conventional petroleum coke filler. The anode characterization data for both conventional and MILDGAS-derived pitch binders were shown in Table 4. The IGT-based anodes met or exceeded the conventional anodes made with similar binder:filler ratios in all of the 10 key performance properties tested except coefficient of thermal expansion (CTE), and even in that case the differences were not statistically significant. The density, strength, and modulus were high, assuring good
Figure 9. EFFECTS OF PITCH:GAS RATIO ON QI, TI, AND COKING VALUE

Figure 10. EFFECTS OF PITCH:GAS RATIO ON C:H RATIO, SULFUR, SPECIFIC GRAVITY, AND SOFTENING POINT

physical integrity of the anode in the smelter, the resistivity was low enough to ensure proper electrical performance, and thermal expansion and conductivity fell within the ranges required to avoid distortions which would lead to cracking under high-temperature conditions. The reactivity of the anodes to CO₂ was less than that of the conventional anodes, and the reactivity to air was virtually
identical. This was true even in spite of the relatively high sulfur content of the pitch.

The MILDGAS-based pitch wetted the coke particles well, and there was no significant development of cracks during baking of the cores. The chemical analyses did not show any unusual contaminants, and even the sulfur content of 1.82 wt% was within the typical range of 1.2-2.4 wt% for anodes made with conventional binders.

These results are extremely encouraging, wherein they show that the thermocracked pitch from mild gasification of Illinois No. 6 coal can perform adequately as an anode binder under test conditions routinely employed by a major potential user (i.e., Alcoa). The acceptance of value-added mild gasification products by industrial users is vital to the commercial success of the process, and must be assured before commercialization can be pursued with confidence.

Task 7. Process Scale-Up Design

A conceptual process flow diagram for the integration of pitch thermocracking with mild gasification has been devised. This is not intended to function as a definitive MILDGAS process diagram, but merely as a preliminary framework for integrating the concept developed in this program into the mild gasification of Illinois coals.

The process flow diagram is shown in Figure 11. The FTC mass and elemental balances were derived from test 7-042294, which produced the best combination of properties for the finished pitch at reasonable yields, and assume that the FTC unit operation includes its own subunits to separate coke and pitch from the product stream. Adjustments were made to the experimental data to produce a 100% balance for all of the major elements (C, H, N, S, O, and ash). The mild gasification material balance was derived from selected test data from the DOE-sponsored technology development program conducted in the 100-lb/h PRU at IGT.

The tar-laden product gas from the mild gasification unit is partially cooled in the Fractionation unit to condense and coalesce the high-boiling (ca. 260°C+) fraction which comprises the crude pitch. That material is conveyed to the FTC unit, where it is converted to binder-quality finished pitch, pitch coke, thermocracker oil, water, and thermocracker gas. The oil- and water-laden gases from both mild gasification and FTC units are sent to a common Liquid
Figure 11. PROCESS FLOW DIAGRAM FOR MILD GASIFICATION WITH PITCH THERMOCRACKING
Separation, where the gas stream is further cooled to condense the remaining oils and water.

For simplicity, the process shown here does not take into account fluidization gases in mild gasification and entrainment gases in the FTC unit. These streams will be incorporated into the design as process data becomes available from the MILDGAS PDU and related MILDGAS commercial plant design data.

The BFD shows that each ton of maf coal will produce about 99 lb of electrode binder pitch and 101 lb of green pitch coke, each of which currently commands a price of $250-$300/ton. Consequently, these two value-added products alone could offset 85% of the cost of the feed coal at a price of about $25/ton. In comparison, mild gasification crude pitch, at a fuel value of only about $35/ton based on heating value, would only offset about $4-$5 of the coal cost. These comments also do not take into account the added value of the oils and fuel gas recovered from the thermocracking step. If it is assumed that the fuel gas is completely consumed to provide energy to the FTC unit, and that the by-product FTC oil (about 39 lb/ton maf feed coal) is salable for chemical feedstocks at the current crude oil price of $18/bbl, the FTC unit can completely pay for the coal feedstock, leaving the other mild gasification co-products -- form coke and chemical feedstocks -- unburdened from the coal cost.
CONCLUSIONS AND RECOMMENDATIONS

Flash thermocracking of MILDGAS crude pitch from Illinois No. 6 coal at 750°-850°C results in a finished pitch which meets binder pitch requirements for QI, TI, softening point, and C:H ratio, and yields a coking value 91% of the typical specification value. Further improvements in pitch density and sulfur are still required, which will be addressed in a subsequent project. The finished pitch yield is about 25-30 wt% when an atomizing spray is used to convey the crude pitch into the reactor. Lack of atomization decreases the pitch yield and increases pitch coke.

Tests performed under 50 vol% H₂/N₂ and under 100% H₂ did not result in any significant reduction in sulfur content of the finished pitch, although some sulfur reduction in the pitch coke was observed. The use of H₂ in the reaction gas, however, had adverse effects on the pitch QI, TI, coking value, and softening point. Therefore, the use of a reducing atmosphere for thermocracking has been abandoned in favor of a neutral atmosphere.

The pitch sulfur content was most influenced by temperature, with the higher temperatures resulting in lower sulfur. With the thermocracker operating at 840°-870°C, the pitch sulfur content was reduced from 2.4 wt% to about 2.0 wt%, regardless of the reaction gas atmosphere.

Increasing the pitch:gas ratio appeared to improve the properties of the finished pitch, in terms of aromaticity, softening point, QI and TI content. The conditions selected to make a production batch of pitch for electrode preparation are: reactor temperature 840°/870°C (top zone/bottom zone), carrier gas 100 vol% N₂, residence time 2.2-2.4 seconds, and pitch:gas ratio 1.10×10⁻⁴ (v/v).

Test anodes were fabricated by Alcoa from our upgraded pitch and conventional petroleum coke filler, and the electrodes' physical and chemical properties were shown to be equal to or better than those of similar anodes made with a conventional premium coal tar pitch.

A conceptual process block flow diagram was produced, including mass and elemental balances, integrating flash thermocracking with mild gasification based on the IGT MILDGAS process. The BFD shows that each ton of maf coal will produce about 99 lb of electrode binder pitch, 101 lb of green pitch coke, and 39 lb of high-BTX oil. These value-added products could offset the cost of the feed coal at a price of about $25/ton. In comparison, the non-upgraded
mild gasification crude pitch, at a fuel value of only about $35/ton based on heating value, would only offset about $4-$5 of the coal cost. So the FTC products can completely pay for the coal feedstock, leaving the other mild gasification co-products -- form coke and chemical feedstocks -- unburdened from the coal cost.

Future work will investigate methods of reducing the sulfur content in the finished pitch, exploring the product potential of the pitch coke, and updating the process flow diagram to include the best available data from sulfur reduction work. It is anticipated that gas recycle streams to the mild gasification and flash thermocracking units will also be included in the updated process flow diagram.

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