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Mild Gasification Technology Development Process
Task 3: Bench-Scale Char Upgrading Study
February 1988 - November 1990

Topical Report

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Work Performed Under Contract No.: DE-AC21-87MC24266

For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, West Virginia

By
Institute of Gas Technology
Chicago, Illinois

DISCLAIMER

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EXECUTIVE SUMMARY

Under U.S. DOE sponsorship, a project team consisting of the Institute of Gas Technology (IGT), Peabody Holding Company, Inc., and Bechtel Group is developing a process for the mild gasification of coal in an isothermal process research unit (PRU) at IGT in Chicago. The IGT process is capable of converting all types of coals to value-added co-products which can open new markets for the U.S. coal industry.

The IGT mild gasification process incorporates an integrated fluidized-bed/entrained-bed reactor with heat supplied by a combination of hot char and gas recycle. The use of mild operating conditions (1000° to 1500°F), low pressures (<50 psig), and continuous operation in closed reactors, combined with the potential value-added benefits from the sale of co-products offer an economical and environmentally sound approach to advanced coal utilization.

Three value-added solid co-products from mild gasification were identified in the Topical Report on Task 1, entitled, "Literature Survey of Mild Gasification Processes, Co-Products Upgrading and Utilization, and Market Assessment".[1] These co-products are a metallurgical form coke, a smokeless fuel, and an activated adsorbent char.

The chars from the mild gasification PRU tests in Tasks 2 and 4 of the program and chars from a laboratory fluidized bed were evaluated with bench-scale performance tests specific for each of the above products. The studies indicated that a form coke briquette made from West Virginia coal char can be of sufficient strength and in the proper range of coke reactivity for metallurgical use. Three-inch-diameter briquettes were made successfully in a single mold and a pilot-scale test was conducted at a briquette production rate of 1000 lb/h. These tests showed that the key process step is the heated mixing step that permits a portion of the volatile material in the binder coal to leave before the plastic mass is compacted in the roll briquetting machine. Larger scale tests will be required to prove the performance of the form coke in industrial equipment, but the major factors of strength and reactivity do not appear to be a technical barrier.

Briquettes of smokeless fuel do not have to be as strong as form coke briquettes. Limestone, which can be easily blended into the char briquettes, has been shown to capture 88% of the sulfur from the char of an Illinois No. 6

coal in simple combustion tests. All of the captured sulfur was in the form of calcium sulfate in the combusted ash residue.

A good quality, low-cost activated adsorbent char was prepared from Illinois No. 6 char by optimizing the carbon burn-off with steam. The adsorbent char was comparable in performance characteristics to a commercial bituminous coal-based activated char and was, in particular, well-suited for adsorption of low molecular weight species.

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OBJECTIVE

The overall objective of this program is to develop mild gasification technology and co-product utilization. The objective of Task 3, Bench-Scale Char Upgrading Study, was to investigate the necessary steps for upgrading the mild gasification char into potential high-market-value solid products. Recommendations of the Task 1 market survey section formed the basis for selecting three value-added solid products from mild gasification char: form coke, smokeless fuel, and activated adsorbent char.

Specifically, the objective of Task 3 was to evaluate the upgraded samples of the char products with standard bench-scale tests to determine and compare the properties and performance of the char products with comparable commercial products.

INTRODUCTION

The U.S. Department of Energy (DOE) is supporting the development of mild gasification technology to produce coal-derived fuels and chemical feedstocks. Mild gasification may be the most affordable route to increase coal utilization in the present economic climate. This technology uses operating conditions of 1000° to 1500°F, near-atmospheric pressure, and inexpensive reactants to convert coal to a slate of co-products.

Mild gasification could be considered an advanced low-temperature coal carbonization process. Low-temperature carbonization of coal was popular in the United States until natural gas became abundantly available, and it is still used on a commercial scale in some foreign countries; however, the old technology has been improved to produce value-added co-products through the application of technical and scientific knowledge about coal conversion that has been developed over the past twenty-five years. Improvements in reactor and process design are being applied to significantly enhance the yield and quality of co-products as well as the overall economics of the technology. Because of the mild operating conditions and process simplicity, mild gasification can use available materials of construction and conventional engineering design and construction practices. As a result, the capital and operating costs are expected to be low. In this context, by successfully developing and marketing the co-products to derive the value-added benefits, it should be possible to commercialize the technology within the next ten years.

With support of the U.S. DOE, a project team consisting of the Institute of Gas Technology, Peabody Holding Company, Inc., and Bechtel Group is developing a mild gasification process that uses a fluidized/entrained-bed reactor. This reactor is designed to process all types of coal over a wide range of particle sizes without oxidative pretreatment, and also without the use of oxygen or air as reactants. Process heat, in the conceptual commercial reactor, would be provided by recycled hot char or high-temperature fuel or flue gases derived from burning a portion of the process-derived fuel gases. The co-product streams consisting of char, fuel gas, water, and oils/ tars would be separated by conventional methods employing cyclones, staged condensers, and recycle-oil scrubbers.

An isothermal process research unit (PRU) has been built at IGT as shown schematically in Figure 1. It consists of an electrically heated 8-inch-ID,

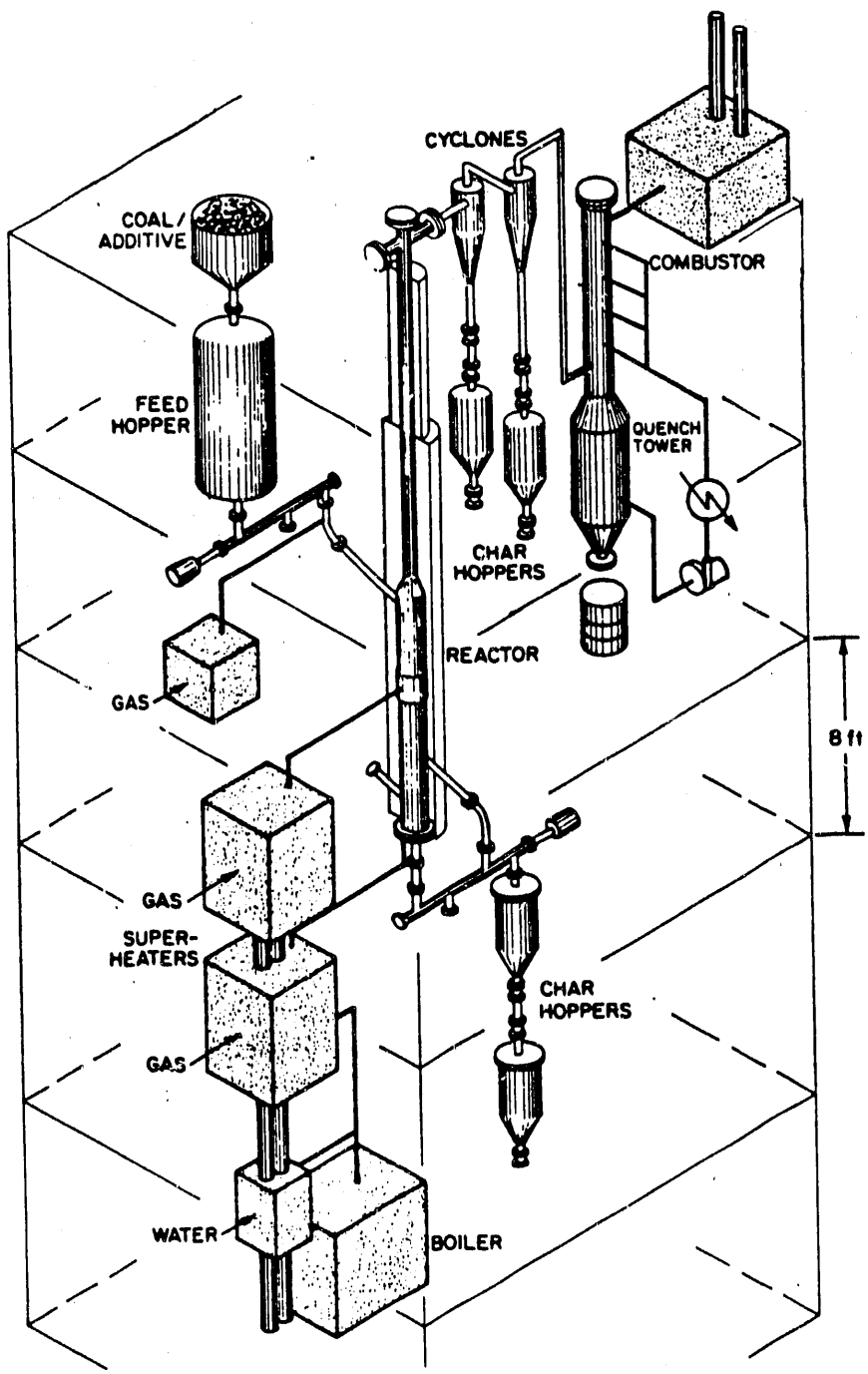


Figure 1. ISOMETRIC OF PRU SYSTEM

8-foot-long fluidized-bed section and a 4-inch-ID, 13-foot-long entrained flow section. Both sections are enclosed in clam-shell electrical heaters. The design coal feed capacity is 100 lb/h, and the coal can be fed either to the fluidized bed or the freeboard region above the fluidized bed and below the entrained section. The stainless steel reactor vessel is designed for operation at a maximum temperature and pressure of 1500°F and 50 psig, respectively.

A detailed description of the PRU, its operation, and mild gasification test results are presented in the Topical report for Task 2 of this project, entitled "Mild Gasification Technology Development, Process Research Unit Tests Using Slipstream Sampling".[2]

PROJECT APPROACH

The mild gasification project consists of four major tasks:

Task 1. Literature Survey of Mild Gasification Processes, Co-Products Upgrading and Utilization, and Market Assessment

Task 2. Bench-Scale Mild Gasification Study

Task 3. Bench-Scale Char Upgrading Study

Task 4. System Integration Studies.

The approach to the development of an advanced mild gasification process was based, in Task 1 of this project, on a detailed literature survey and review of the state-of-the-art technology for coal conversion to readily saleable co-products. A market survey, conducted concurrently with the literature survey, identified the value-added priority end uses of the co-products. This information was used to determine the basis for design of the type of reactor, the process operating conditions, and the methods of co-products upgrading. The results of the above approach were presented in the Topical Report on Task 1 of this project entitled, "Literature Survey of Mild Gasification Processes, Co-Products Upgrading and Utilization, and Market Assessment".[1] The objective of Task 2 of the project, Bench-Scale Mild Gasification, was to design, build, and operate an isothermal 1.2-ton/day (100-lb/h) process research unit (PRU) with slip stream sampling to determine process performance and to obtain design information for process scale-up. The objective of Task 3, Bench-Scale Char Upgrading, was to evaluate the performance of upgraded samples of potential high-market value solid products. In Task 4, System Integration Studies, a full-stream product gas condenser was designed, built, and operated to obtain the integrated PRU system performance data. Included in this task is the preparation of a process design, including material and energy balances, for a 24-ton/day adiabatic process development unit (PDU) to be erected at Southern Illinois University-Carbondale.

Summary of Potential Markets for Mild Gasification Char Co-Products

The topical report for Task 1 of this program, entitled "Literature Survey of Mild Gasification Processes, Co-Products Upgrading and Utilization, and Market Assessment"[1] identified several large potential markets for value-added mild gasification char co-products. These large markets are as follows:

- Metallurgical form coke (about 30 x 10^6 ton/yr)
- Smokeless fuel (about 50 to 100 x 10^6 ton/yr)
- Activated char (about 1 to 2 x 10^6 ton/yr).

The identification of these co-products was also guided by the technical considerations for the development of the mild gasification process and its integration with coal preparation technology. In addition, the impact of a wide variety of upstream solid processing steps and downstream processing steps were considered for the production of commercial quality liquid and solid co-products. As a result, the mild gasification process that evolved favored a minimum of processing steps.

Developmental work will be required to prepare commercially acceptable products identified from the mild gasification char. The mild gasification process along with downstream processing could be integrated with a coal preparation plant. The feed coals tested in this program came from the high moisture fines (-1/4 inch) stream from Peabody's coal preparation plants that normally mix these fines with the lump coal shipments.

The use of the mild gasification char co-product for the large steam or utility fuel market is technically possible, but because the char as a utility fuel may not have a significant value-added advantage, that market was not evaluated in detail at this time.

Form Coke

A form coke product from the mild gasification char has two sub-markets. The larger of the two markets for form coke is in blast furnace production of iron with a current annual consumption of about 27 million tons of coke per year. A smaller market of about 1.8 million tons per year exists for foundry coke used in cupolas for re-melting and alloying iron to make special steels. The cost of coke from various suppliers is currently about $150 per ton.[3] Consequently, a suitable form coke from mild gasification would present an excellent value-added product. In addition, the mild gasification process offers continuous form coke production with superior environmental control that is difficult and costly to achieve in existing coke oven batteries.

The existing coking plants in the United States are also aging, and environmentally acceptable methods to rapidly produce supplementary supplies

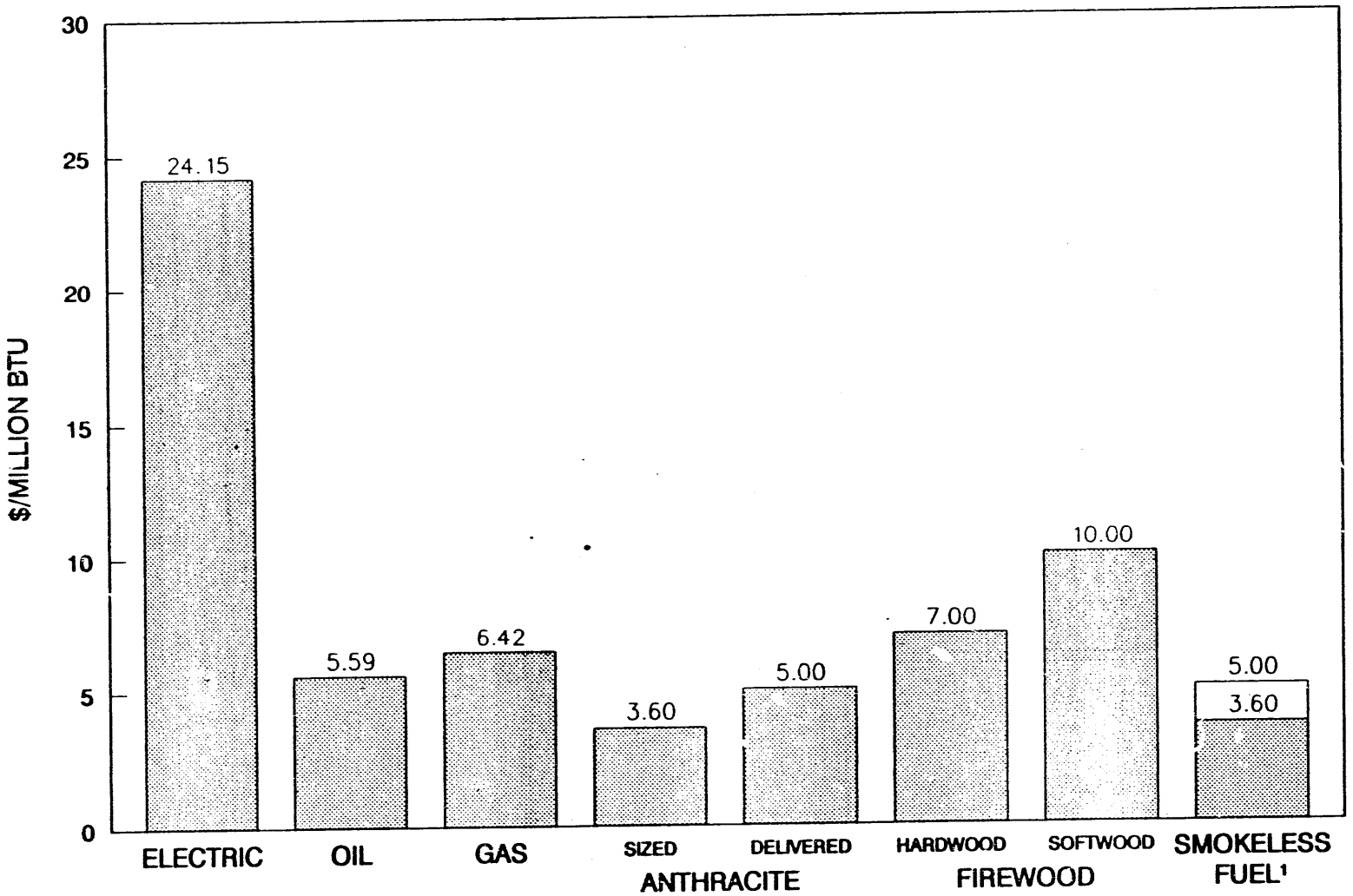
of coke are urgently needed. The replacement coke could come from imports, although this source would not be assured as a long-term supply. The U.S. foundry industry is in a similar situation with lost coking capacity. An assured domestic supply of form coke from a continuous, environmentally safe process would have significant benefits for the steel and coal companies and the nation.

Form coke made from mild gasification char can meet the requirements for coke properties. In general, coke needs a strength sufficient to support the burden in the blast furnace and also has to provide a certain bulk porosity for gas, liquid metal, and flux flows. In addition to these properties, the coke must also meet a reactivity criterion based on its reaction with carbon dioxide, and its sulfur and ash contents should be low. Blast furnace coke is usually produced in the coke oven by selectively blending several coking coals, usually a high volatile and a low volatile coal, to make a strong structure with a desired reactivity. Mild gasification chars can be produced and blended in a similar manner with better control of the process conditions and emissions than attainable in coke ovens.

The properties of foundry coke differ from blast furnace coke, but the char from mild gasification could be processed to satisfy the required criteria. A higher porosity and reactivity are more important than strength in a cupola because the foundry coke is a source of both heat and carbon for transfer into the iron melt to make various steels. A form coke for foundry applications could also incorporate metallic fines such as silicon and manganese that are normally added in the cupola for alloying with the steel. This would enhance the value of foundry form coke significantly by providing a secondary benefit in improving cupola operations.

Smokeless Fuel

The low, yet ignitable volatile matter content of about 10% makes mild gasification char a suitable feedstock for producing briquettes of smokeless fuel. In the case of higher sulfur coals, limestone can be incorporated into the briquette to control the sulfur emissions during combustion. Domestically, the smokeless fuel could be used in place of firewood or, in some localities, anthracite coal. Figure 2 compares the relative ranges of costs of various domestic fuels with the estimated cost of a smokeless fuel product. The smokeless fuel cost is comparable to that of anthracite coal.



¹ Priced competitively with anthracite depending on market conditions

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Figure 2. COMPARISON OF DOMESTIC FUELS

The heating value comparison of the solid fuels is given in Table 1.

Table 1. HEATING VALUE COMPARISON OF SMOKELESS FUEL WITH SOLID FUELS

	Heating Value (million Btu/ton)
Wood (15% moisture)	14.6
Utility Bituminous Coal	21.1
Anthracite	21.6
Charcoal Briquettes	30.0
Smokeless Fuel With Limestone	20.0

When calculated on a heating value basis, the domestic consumption of firewood would be equivalent to about 50 million tons of smokeless fuel. There is no current domestic use of smokeless fuel but demand could materialize if restrictions are imposed on the use of firewood for environmental protection. Additionally, the present export market for smokeless fuel could be significant. Countries with a shortage of firewood, anthracite, or natural gas are candidate markets. Another possible market is represented by countries with district heating central boilers. Korea has imported anthracite from the United States at a cost of about $100 per ton, which includes about $30 per ton for shipping. Smokeless fuel in the United Kingdom was recently being sold for $170 per ton from the Rexco process. This market presents a good potential for a smokeless fuel co-product from mild gasification.

Activated Char

Mild gasification chars could be steam-treated to produce a low-cost activated char product in a powdered or granular form. Commercial adsorbent carbons are made from a variety of carbonaceous materials, including coal, and sell for up to $2000 per ton. Powdered adsorbent forms are generally mixed directly with a contaminated liquid streams for purification; the granular forms are used in packed-bed applications. Currently, major uses of activated carbon include treatment of effluent streams in the paper and pulp industry and treatment of refinery activated sludge. The demand for activated carbon will increase if stricter clean water standards are imposed, and with the

probable appearance of natural gas-fueled urban vehicles, which would use active carbon for fuel storage. The market size is small at present, but with stricter water standards or other events and a competitively priced absorbent carbon, the demand could increase suddenly. A mild gasification process could provide a potentially lower-cost activated char for these applications.

Char Upgrading Studies

Form Coke

The suitability of the granular char from the mild gasification process to be made into form coke was investigated in two bench-scale briquetting studies followed by a pilot-scale production of pillow-shaped briquettes. The investigation was limited to the production of briquettes using only coal as the source of the binder material rather than the higher market-value pitch co-product. First, small 1-inch-diameter by 3/8-inch-thick briquettes were made with the mild gasification chars and tested for strength and coke reactivity. Several 3-inch diameter by 1-inch thick briquettes were then made in a larger mold, focusing on the best conditions to produce a strong briquette. Lastly, a large quantity of 1 by 1.75-inch pillow briquettes were made at a rate of one ton per hour with equipment at a test facility of a manufacturer of roll briquetting equipment.

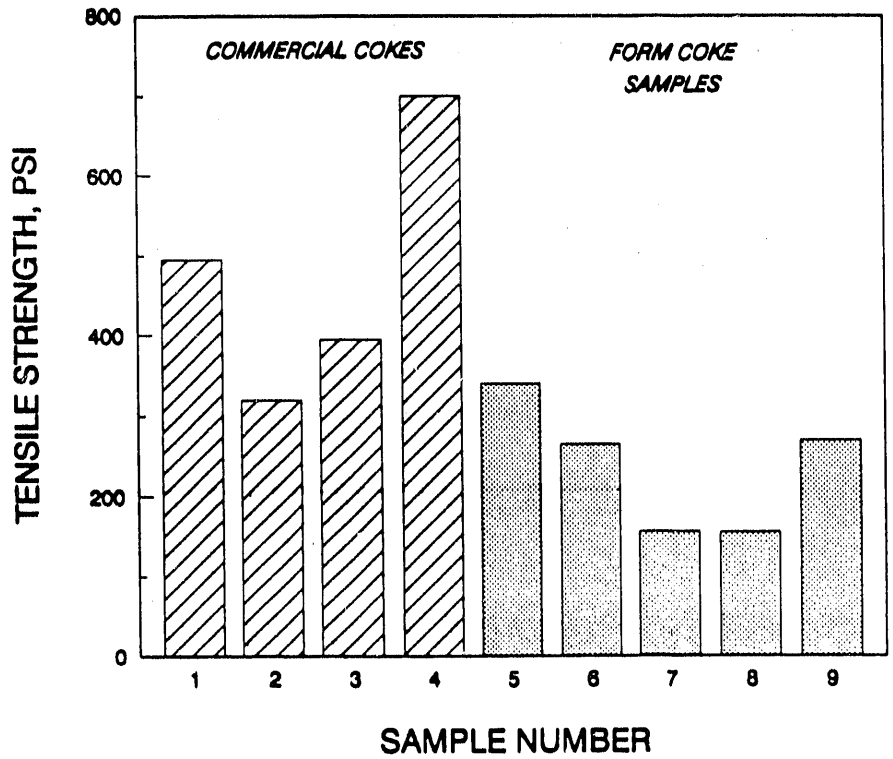
The first test briquettes were made in a one-inch diameter cylindrical mold with chars from the 8-inch-ID mild gasification process research unit (PRU) tests performed in Task 2 of this program. The chars from Illinois No. 6 coal in PRU Tests MG-9 and MG-17 were mixed in a 1:1 weight ratio with the parent coal and pressed in a one-inch diameter mold at 1000°F. Two briquetting pressures, 4,000 and 10,000 psi, were selected to produce the approximately 3/8-inch-thick briquettes. The briquettes were removed from the mold and calcined in an oven under nitrogen up to 1800°F to remove the remaining volatile matter and complete the form coke briquetting process. To test the physical strength of these briquettes, a diametral compression test apparatus was used. The test actually measures the tensile strength up to fracture. The tensile strength tests were conducted on an Instrom (Model 101) compression-tension measuring machine following the procedure of ASTM Test B-485-76.

The range of values of the measured tensile strengths of the various briquettes that were made under various conditions are shown in Figure 3, along with the value measured on a similar sized sample of metallurgical coke obtained from Inland Steel Company and literature values for commercial metallurgical coke and foundry coke. As indicated in Figure 3, the initial briquettes that were made under non-optimized conditions do approach the values for commercial cokes. With optimization of the steps in the briquetting process, it is expected that mild gasification char can be briquetted using coal as a binder material to meet the required physical strength.

In addition to the physical strength, another property of coke important to blast furnace operation is its reactivity value. The reaction rate of the carbon in the coke with the carbon dioxide present in the blast furnace gases is directly related to the iron production rate, because this reaction generates the reductant carbon monoxide. This reactivity value was measured with a briquette made from the mild gasification char using the West Virginia coal. A reactivity test procedure obtained from the Bethlehem Steel Company[4] specifies grinding the coke to 18 x 40 mesh and placing a weighed sample in a quartz tube. The sample is heated to 1825°F under nitrogen and then the nitrogen is replaced with carbon dioxide and held at temperature for 2 hours. The percent weight loss of the coke after 2 hours is correlated with acceptable blast furnace performance.

This procedure was applied and was calibrated with a coke sample obtained from Inland Steel Company that was known as a low-reactivity coke. The resulting value is plotted in Figure 4, which also shows the ranges of industry-accepted low, medium, and high reactivity coke values. The test briquette made with the West Virginia char yielded a medium reactivity value. Current practice of coke production involves blending different coals to achieve the required coke properties and thus, coke reactivity values could be adjusted by blending different coals.

Tailoring of the properties of the form coke briquettes will be an important feature of any candidate char-producing and briquetting process. The major factors that affect both the strength and reactivity of form coke are the density, porosity, voidage, and the type of metallurgical coal or coals. Foundry coke for iron and steel remelting, for example, requires different properties than blast furnace coke. Foundry coke has to be a



SAMPLE NO.	DESCRIPTION	BRIQUETTING PRESSURE (PSI)
1	COMMERCIAL COKE A	---
2	COMMERCIAL COKE B	---
3	FOUNDRY COKE	---
4	INLAND STEEL COKE SAMPLE	---
5	HOT BRIQUETTE (-6 MESH MG-9 CHAR)	4000
6	HOT BRIQUETTE (-6 MESH MG-9 CHAR)	10000
7	HOT BRIQUETTE (20x60 MESH MG-17 CHAR)	4000
8	HOT BRIQUETTE (20x60 MESH MG-17 CHAR)	10000
9	HOT BRIQUETTE (-20 MESH MG-9 CHAR)	4000

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Figure 3. DIAMETRAL COMPRESSION TESTS FOR TENSILE STRENGTH

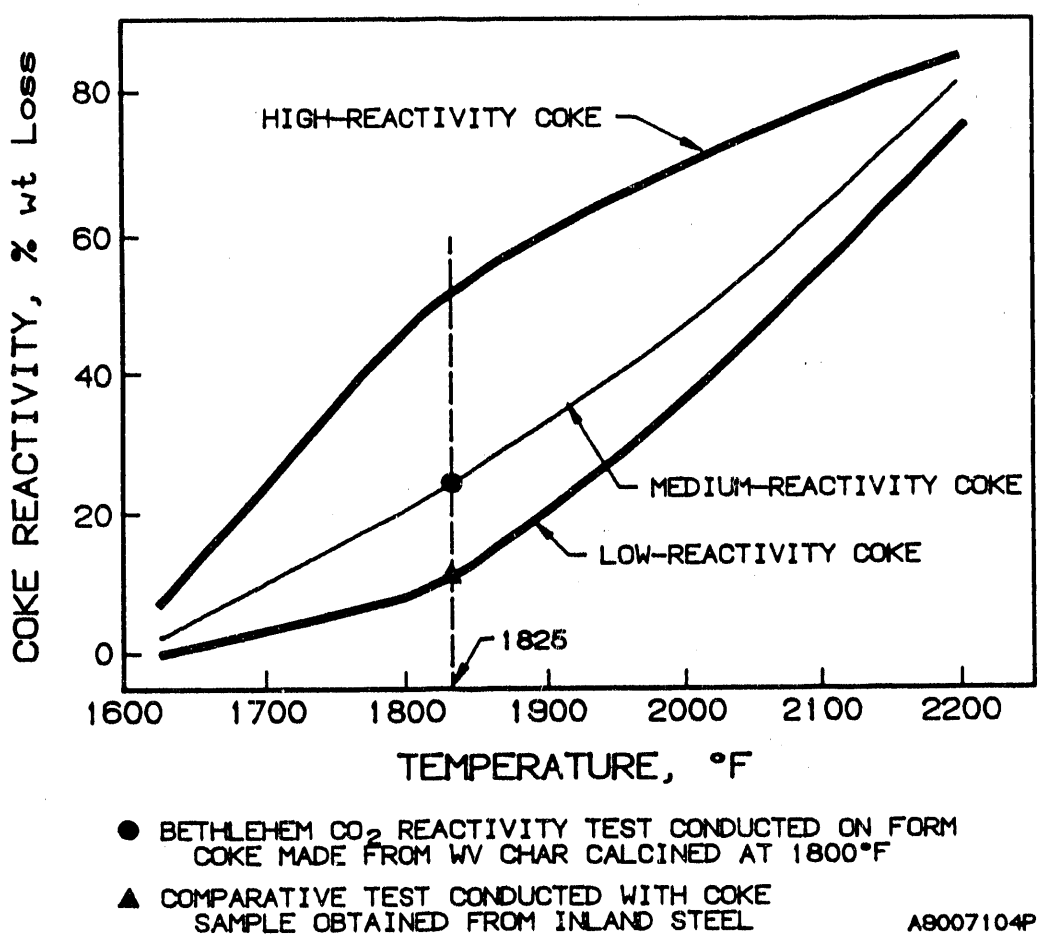


Figure 4. FORM COKE REACTIVITY TESTS

source of heat for melting iron and also a source of carbon for solution into the iron. Consequently, the rate of reaction with carbon dioxide is not as important as in blast furnaces. Blending of fine particles of alloying materials into the foundry coke would increase its value. In another application, coke for rock wool cupola melting is required to be strong to support its burden, but the coke combustion rate, with minimum generation of fines, controls the production rate of the melt, which is spun into fibers.

To make practical sizes of form coke for proof-of-concept testing, a 3-inch diameter mold was machined to make larger briquettes from the West Virginia char. A hydraulic press with heated platens was used to apply the heat and force to the mold. Slight variations to the procedure of heating up to 1000°F, holding at temperature to allow volatiles to leave, and pressing the hot char-coal mixture were practiced until conditions were found to make a strong, dense briquette. The critical step that was identified was the time required for a portion of the volatilized products from the binder coal to leave. If the products do not leave, then the briquette will expand too much upon subsequent calcination. Also, compaction pressures of only about 1000 psi were found to be sufficient for this hot, partially devolatilized plastic mixture. Compression values up to or greater than 20,000 psi have been indicated in some briquetting operations but may not be necessary. The 3-inch briquettes were as strong as the Inland Steel Company sample, and the briquette density was measured as approximately 65 lb/cubic foot, which is comparable to the density measured for the Inland Steel Company coke sample, 62 lb/cubic foot.

With the experience of making the test briquettes, arrangements were made for the production of a large quantity of form coke briquettes from approximate 700 pounds of West Virginia char that was available from the longer-duration mild gasification tests conducted in Task 4 of the program. The char, when blended with about 700 pounds of West Virginia coal, could provide about 1000 pounds of calcined briquettes.

A manufacturer of roll briquetting equipment with a hot briquetting test system that could make pillow briquettes at a rate of about one ton per hour was located. A schematic of the equipment, which is located at K. R. Komarek Research in Anniston, AL, is shown in Figure 5. The pre-mixed char and coal were fed to the buffer hopper, and then pneumatically conveyed up the flash

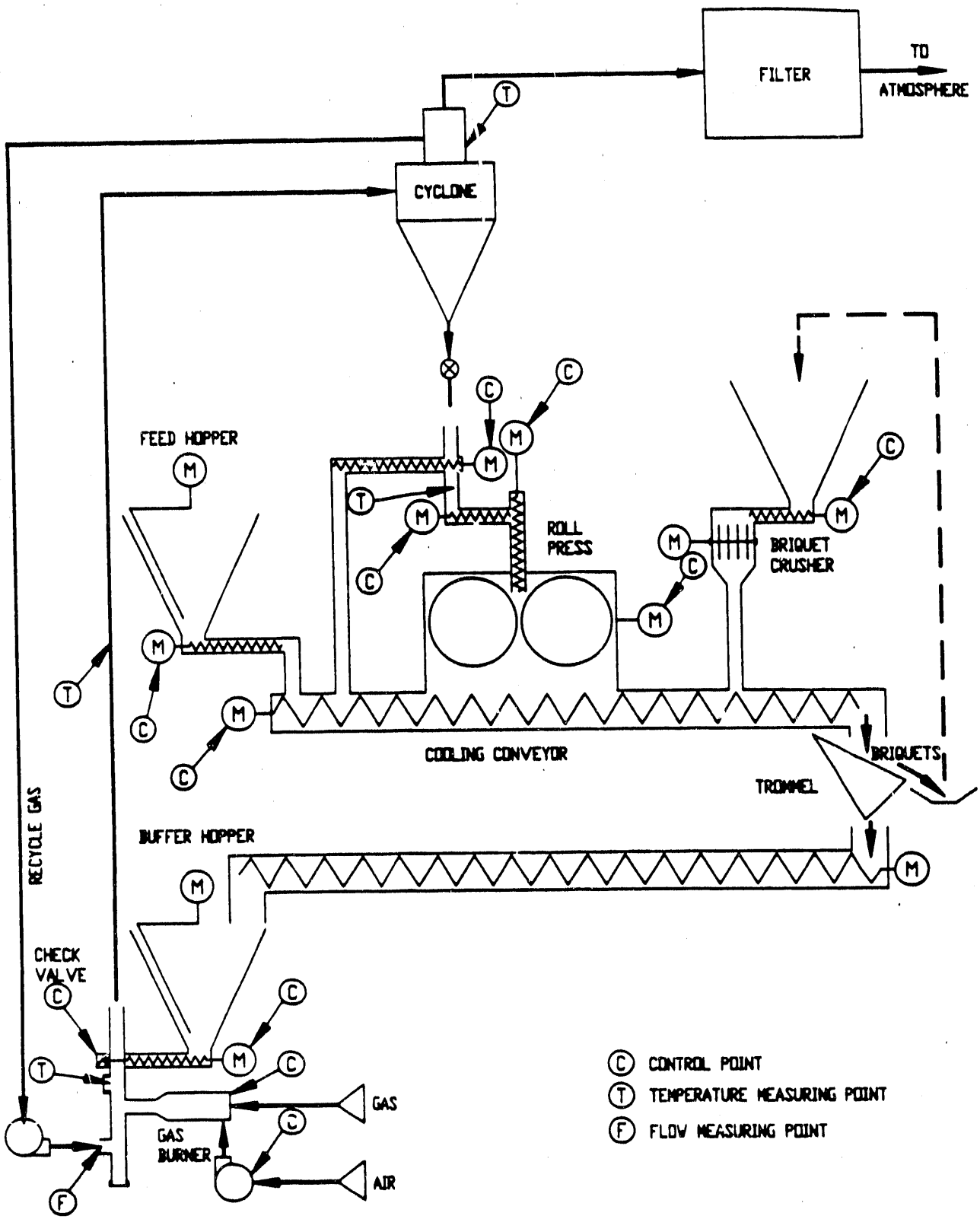


Figure 5. SCHEMATIC PROCESS FLOW DIAGRAM OF HOT BRIQUETTING INSTALLATION

dryer-heater section to the cyclone and fed directly to the roll briquetting press. The roll briquetting press had dies to make 1- by 1.75-inch pillow briquettes.

Prior to the operation of the briquetting test unit, several batch briquetting tests were conducted in other similar roll briquetting machines to identify settings for the required roll compaction pressure and the feed rate to the rolls. One variation of the coal-to-char mix ratio, from 1:1 to 0.75:1 by weight coal to char, was investigated. The ratio with less coal seemed to produce an equally strong briquette, but available time precluded more detailed investigation of the mix ratio. The mixtures could only be batch-heated in an oven to about 400°F in these preliminary trials, but briquettes of good green strength were produced that survived a six-foot drop test intact. Although the mixture temperature was below the approximately 900°F that is required to release volatile matter for maximum briquette compaction and strength, these tests scoped out the operating parameters for the roll briquetting system shown in Figure 5.

After the operating parameters were defined, the 700 pounds of West Virginia char was mixed with 700 pounds of the coal to begin feeding to the hot briquetting system. However, the test system heater could only achieve a mixture temperature of about 550°F at the entrance to the rolls because of excessive heat losses. Efforts to increase the temperature were not successful, and about 600 pounds of briquettes were made before the operation was stopped. A screw conveyor used in the equipment to transport the briquettes to the receiving box broke about one-third of the briquettes in half. A screen belt conveyor would be the preferred conveyor for the briquettes.

About 200 of these pillow briquettes were heated to 1000°F to release the volatile matter in the coal binder. The temperature was then raised to 1800°F to complete the calcination. Because the volatiles were not released prior to briquetting, the briquettes expanded, nearly doubling their volume. The measured density of the briquettes was 22.5 lbs/cubic foot, which is about one-third of that of the good 3-inch briquettes. The pillow briquettes did not fracture in a six-foot drop test, and showed a 3% weight attrition in an ASTM-D-3038-83 drop shatter test for coke. However, about 75% of the briquettes crumbled in a ASTM D-3402-81 tumbler test for coke which tumbles the coke for 1400 revolutions.

Measurement of the carbon dioxide reactivity of the calcined briquettes indicated a 40% weight loss in the Bethlehem Steel coke reactivity procedure, which places the briquettes near the high reactivity range of coke values on Figure 4. The low density and high porosity of the calcined pillow briquettes contributed to an increase in the weight loss as measured by the two-hour carbon dioxide reaction test.

These studies have shown that the crucial step in the briquetting process for form coke production is the char and coal mixing step at a temperature from 800 to 1000°F, depending on the time required for the release of a portion of the volatile matter, and not the actual briquette formation in the rolls. The single 3-inch-diameter briquettes were made in a near-optimum way and were as strong as the coke sample from Inland Steel. However, where this strength level is not required, such as in smokeless fuel briquettes, the key step would involve blending of additives to control the release of sulfur and assurance of a minimal volatile matter content for ignitability.

Smokeless Fuel

The bench-scale tests to evaluate the production of smokeless fuel involved preparation of briquettes from mixtures of Illinois No. 6 coal char, limestone, and about 12% pitch. Binderless briquetting could also be performed without pitch addition. The briquettes were made in the one-inch diameter mold under briquetting pressures of 4000 and 10,000 psi. Pitch was used for these briquettes as an expedient procedure to make the smokeless fuel samples. Two different limestones were used, a pure grade of limestone and a dolomitic limestone. The analyses of these additives are shown in Table 2. These were added to the char mixture to provide a calcium-to-sulfur molar ratio of 2:1 in the briquettes. The briquettes were then subjected to a low temperature curing step at 400°F to polymerize and harden the binder.

In the combustion tests, the briquettes were stacked in a small pile and combusted in a muffle furnace at about 1560°F. The 10 to 15% volatile matter content of the char was sufficient for ignition and combustion of the briquettes. The ash residues from the top of the pile and from the center of the pile were analyzed for calcium sulfate and other sulfur forms to assess sulfur retention. The test results show that the two limestones retained nearly the same quantity of sulfur in this simple combustion test.

Table 2. ANALYSES OF LIMESTONES USED IN SMOKELESS FUEL BRIQUETTES

Component, wt%	Pure Limestone	Dolomitic Limestone
Calcium	39.1	34.0
Magnesium	0.55	3.7
Potassium	0.5	0.33
Iron	0.09	0.16
Aluminum	0.05	<0.1
Silicon	0.1	0.78
Strontium	0.016	0.021
Carbon Dioxide	44.6	43.5
Oxygen (by difference)	14.994	17.409
Total	100.000	100.000

Figure 6 shows the various sulfur forms and retention levels before and after combustion with 84 and 88% of the sulfur being captured from the center and top of the pile, respectively. Of the sulfur retained, 99% is in the form of calcium sulfate, which is suitable as a non-leachable landfill material.

The heating values of the smokeless fuel briquettes from Illinois No. 6 coal-derived char with limestone were compared in Table 1 in the previous section with the heating value of other possible solid fuels. It is apparent that the heating value of smokeless fuel from mild gasification char compares favorably with the heating values of common domestic heating fuels.

Activated Char

The potential for producing a low-cost activated adsorbent char was explored by steam-treating a number of mild gasification char samples from Illinois No. 6 coal and measuring their physical and adsorbent properties. The mild gasification char was produced in the 8-inch-ID process research unit (PRU) and also in a 2-inch-ID laboratory-scale reactor. The char activation was accomplished in a separate 2-inch-ID activation reactor. The chars were activated using steam for varying periods of time to determine the effects of the extent of activation on the resulting char properties and performance.

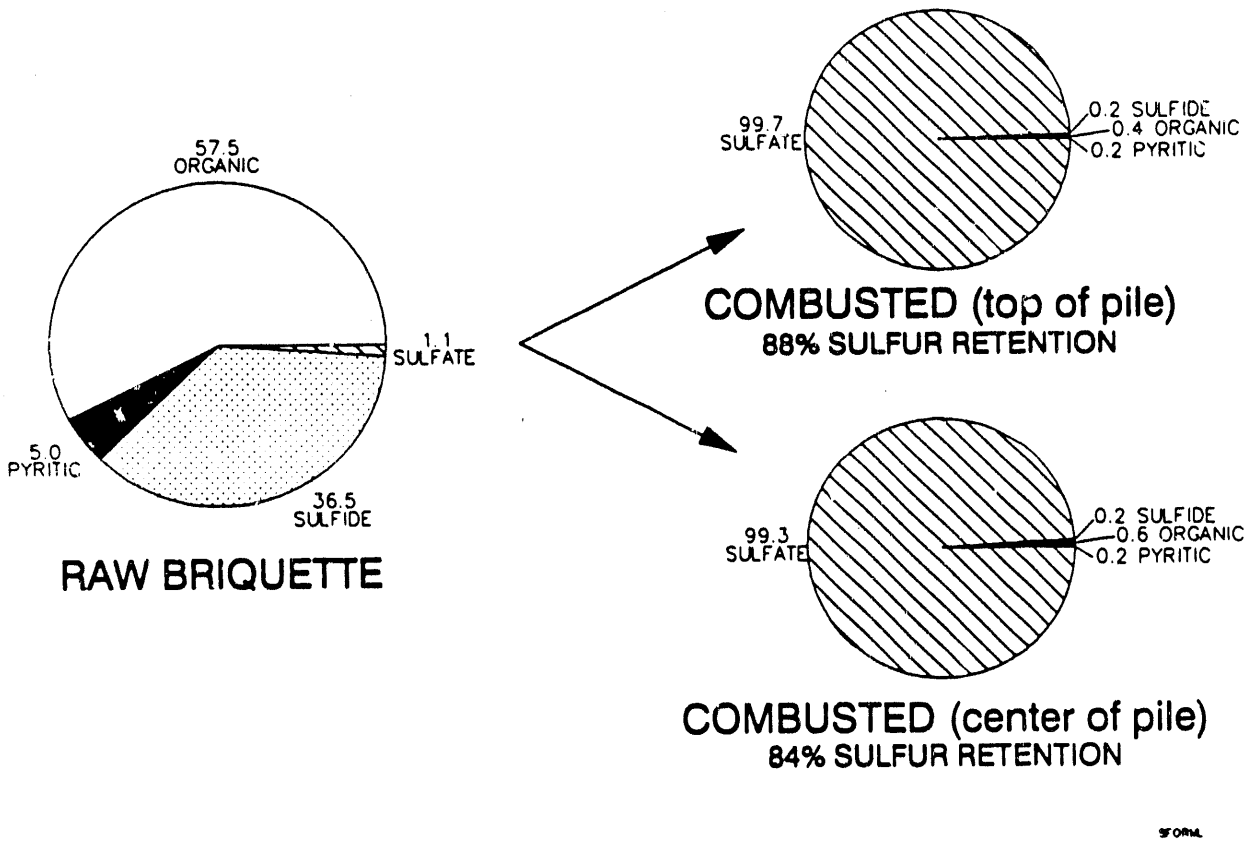


Figure 6. SULFUR FORMS IN COMBUSTED SMOKELESS FUEL

Char Sample Preparation Procedure

Because the mild gasification char samples from the PRU contained a portion of the coke breeze diluent used in the feed, a 2-inch-ID fluidized bed reactor as shown in Figure 7 was constructed to prepare the char samples used for the adsorbent char studies. The following procedure was used to prepare the char to simulate the mild gasification PRU. Approximately 200 grams of coal was loaded into the feed hopper which was fed to the reactor fluidized with nitrogen. When the reactor achieved 1200°F, the entire contents of the feed hopper was fed to the reactor and fluidized for 15 minutes to simulate the residence time in the PRU. The resulting char was transferred into the char collection hopper.

The 2-inch-ID reactor has a slanting gas distribution cone. A high center-jet velocity is maintained to maximize agitation to prevent agglomeration and de-fluidization with the caking Illinois No. 6 coal. However, agglomeration occurred in the operation of this unit with 100% coal feed, as expected. For the purpose of this task to study the upgrading of the char, the coal was subjected to a light air-oxidation treatment at 300°F prior to mild gasification. This reduced the agglomeration in the reactor so that char samples could be produced for further tests.

Char Activation Procedure

The fluidized-bed steam-treatment apparatus used to activate the char samples is shown in Figure 8. The activation temperature of 1560°F was chosen based on work by Klose and Born[5] who found that iodine adsorption numbers of activated carbons peak at an activation temperature of about 1470°F, while surface areas peak at a higher activation temperature of about 1650°F. The activation temperature of 1560°F was selected as a midway point The char activation procedure involved placing about 100 grams of char in the reactor and heating it to temperature under a purge flow of nitrogen. A flow of nitrogen and steam sufficient to fluidize the char was then maintained for different periods ranging from 45 to 240 minutes for varying degrees of carbon conversion.

Adsorbent Characterization Methods

The performance of an activated carbon depends upon a number of different parameters which include surface area, hardness, pH, apparent density, particle size, pore size distribution, adsorptive capacity of standard

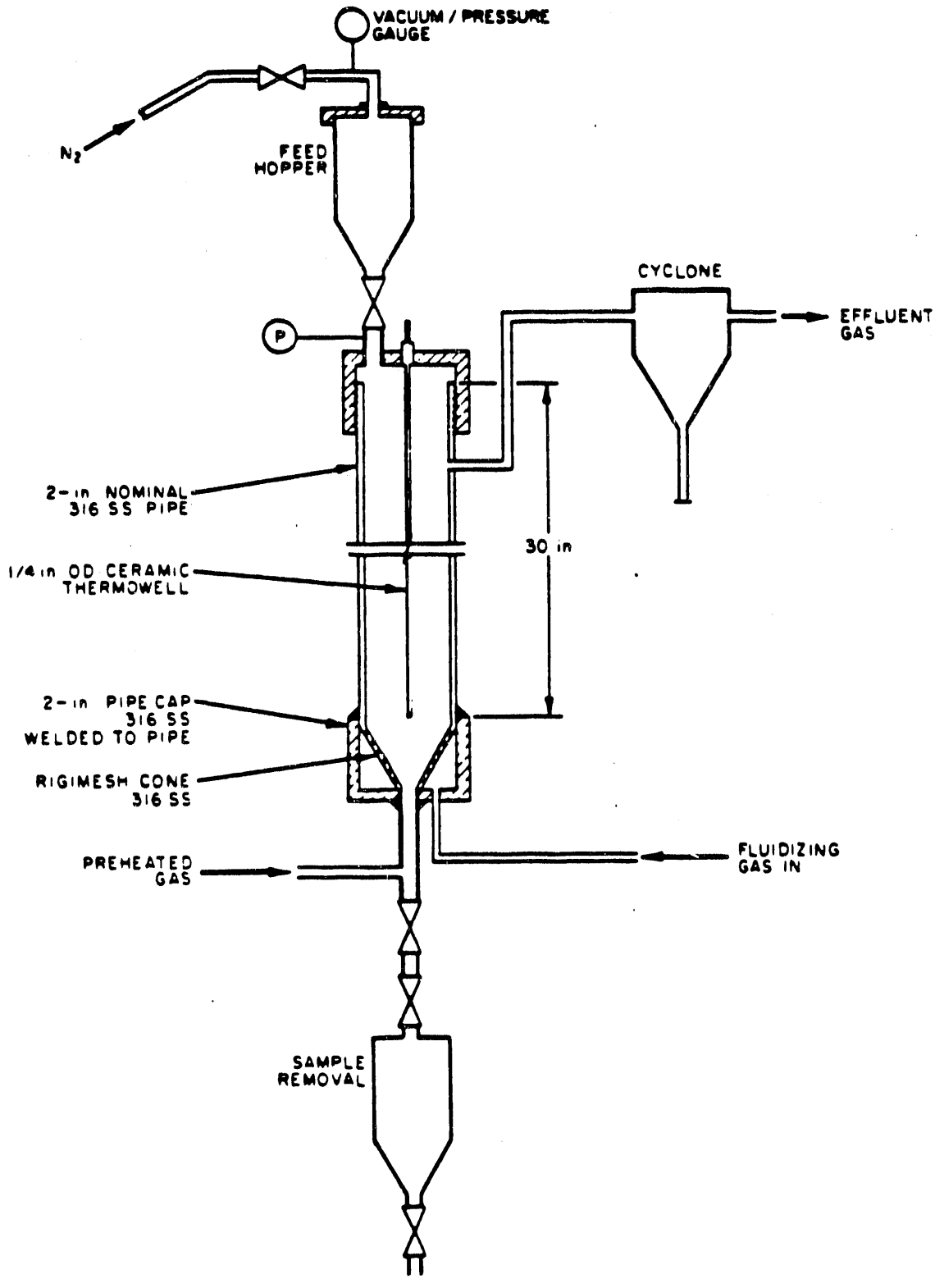


Figure 7. SCHEMATIC DIAGRAM OF THE 2-INCH-ID FLUIDIZED-BED REACTOR

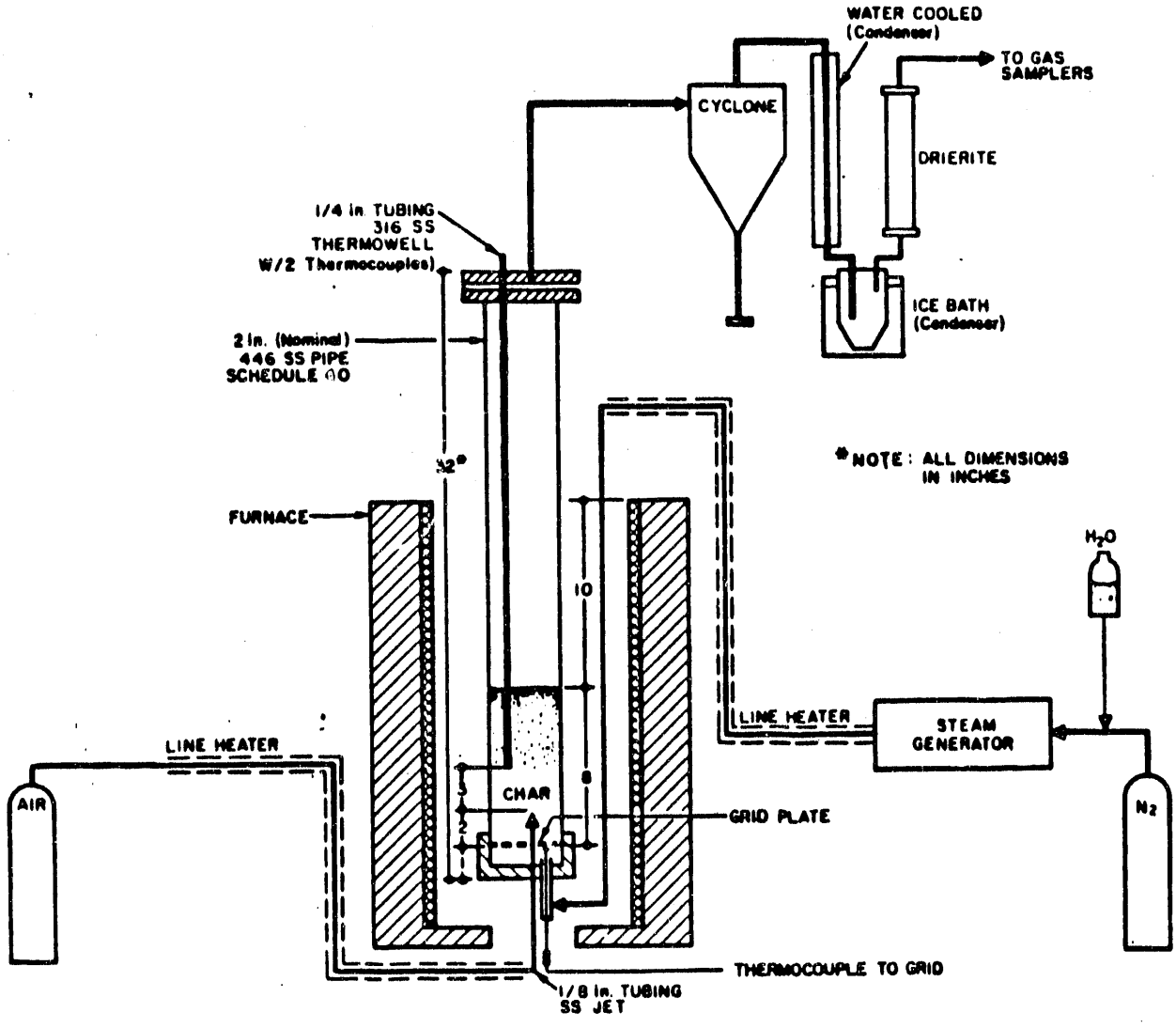


Figure 8. SCHEMATIC DIAGRAM OF THE FLUIDIZED-BED STEAM TREATMENT APPARATUS

chemicals, and kinetic/mass transfer coefficients. Table 3 lists the tests and methods used to analyze selected activated char properties. ASTM standard methods were used whenever applicable to characterize the char. There is no ASTM method to characterize extractable material from the activated carbon, so the standard extraction procedure (EP) was used.

Table 3. STANDARD TESTS FOR ACTIVATED CARBON

Property	ASTM Test Method
Char, Ash, Sulfur	D 3172-73, D 3176-84
Apparent Density	D 2854-70
Hardness	D 3807-79
Iodine Number	D 4607-86
pH	D 3838-80
Particle Size Distribution	D 2862-70
EP Toxicity	N/A

The surface area and porosity of the adsorbents were determined using the standard BET method with a Micrometric Model 2100 D surface area and pore-volume analyzer. This test equipment uses both nitrogen and mercury to measure the range of pore diameters from 10 to over 200 Angstroms.

Adsorption isotherms were measured with a procedure of washing, drying, and grinding the chars before contacting various amounts of char from 0.01 to 2 grams with a solution of 3,5-dichorophenol (DCP) or 3,5-dimethylphenol (DMP) for a period of six hours. The char was then separated by filtration and the concentration of the solutions were determined by a UV absorption apparatus.

For batch kinetic tests measuring adsorption rates, similar quantities of char were placed in the solutions and stirred. Solution samples were periodically withdrawn and the concentrations were measured with the UV absorption apparatus. The solutions of DCP and DMP were chosen to represent phenols in wastewater from many types of industrial plants. In these tests, an activated carbon was purchased from Calgon Company (Type OL bituminous coal based) and tested for comparison to the char samples.

Discussion of Test Results

The objective of these tests was to investigate the method of producing an adsorbent from mild gasification char that has the maximum adsorptive capacity, as determined by iodine adsorption and surface area values, with the minimum amount of activation in terms of carbon burnoff. Once the optimum activation procedure was identified, a larger batch of char was prepared for the selected adsorbent performance tests. A number of evaluation tests were first conducted with the mild gasification chars from the PRU and from the 2-inch reactor to determine the optimum activation conditions before specific performance tests were made. Table 4 lists the test char samples and resulting search data.

The first two tests listed in Table 4 used char from PRU Test MG-6. In Test 1-23A the char was steam-treated at 1652°F and in Test 1-28 the treatment temperature was 1562°F. The iodine adsorption numbers measured for these activated chars, each with a similar degree of carbon burnoff, were 525 and 596, respectively. Commercial grade adsorbents are expected to achieve iodine numbers up to about 1000. The next two tests were conducted with char from PRU Test MG-9. The carbon burnoff amounts achieved in Tests 1-40 and 1-45 were different and iodine numbers of 464 and 348 were measured for the MG-9 char with 47 and 30 percent carbon burnoff, respectively. One difference between the MG-9 char and the MG-6 char was that the MG-9 char had a lower carbon content and a higher ash content than the MG-6 char, resulting from a greater degree of conversion in the PRU.

The remainder of the test chars in Table 4 were prepared in the 2-inch reactor after a minimum air-oxidation pretreatment step and steam treated at 1562°F for different lengths of time. The char for Test 1-50a was air-oxidized overnight at 300 °F for a greater degree of pre-treatment. The resulting activated char in Test 1-50a shows a high iodine number but also a high carbon burnoff value compared to the other test chars. The char in Test 2-29c was made from a less oxidized coal with a similar carbon burnoff level. It resulted in an iodine number similar to that of the highly pretreated coal used in Test 1-50a, but a lower surface area value than that of the more oxidized coal. An air oxidation pretreatment of caking coals is not desired for mild gasification, as the liquid yields are adversely affected. It is employed here as an experimental expedient for the preparation of controlled property chars.

Table 4, Part 1. SUMMARY OF RESULTS FROM CHAR ACTIVATION AND ADSORPTION TESTS

Test Number	1-23A	1-28	1-40	1-45
Char Source	MG-6	MG-6	MG-9	MG-9
Feed Char Composition (Dry), wt %				
Carbon	68.30	68.30	62.93	62.93
Sulfur	2.67	2.67	3.53	3.53
Ash	21.64	21.64	28.46	28.46
Activation Temperature, °F	1650	1560	1560	1560
Duration of Activation, min	60	100	150	127
Activation Gas Composition, vol %				
Nitrogen	71.7	71.8	79.7	79.7
Steam	28.3	28.2	20.3	20.3
Percent Carbon Burn-Off	43	40	47	30
Activated Char Properties				
Ultimate Analysis, wt %				
Ash	ND	31.24	ND	ND
Carbon	ND	63.83	ND	ND
Hydrogen	ND	0.38	ND	ND
Nitrogen	ND	1.06	ND	ND
Sulfur	ND	1.69	ND	ND
Oxygen	ND	1.80	ND	ND
Ball Pan Hardness Number	52.2	51.1	46.1	--
Apparent Density, g/ml	0.27	0.27	0.32	0.29
Sieve Analysis, mesh				
+6	--	--	--	--
-6+12	13.3	ND	22.82	ND
-12+20	29.4	ND	15.72	ND
-20+40	32.8	ND	14.28	ND
-40+60	19.8	ND	18.74	ND
-60+80	3.2	ND	18.81	ND
-80	1.6	ND	9.81	ND
Surface Area, m^2/g	--	563	--	--
Iodine Number	525	597	464	348

ND = Not determined.

Table 4, Part 2. SUMMARY OF RESULTS FROM CHAR ACTIVATION AND ADSORPTION TESTS

Test Number	1-50A	2-11	2-29A	2-29B
Char Source	P-1A	P-1B	P-2	P-2
Feed Char Composition (Dry), wt %				
Carbon	70.20	61.53	73.52	73.52
Sulfur	2.87	2.88	2.38	2.38
Ash	22.06	28.99	17.89	17.89
Activation Temperature, °F	1560	1560	1560	1560
Duration of Activation, min	120	120	45	90
Activation Gas Composition, vol %				
Nitrogen	74.2	76.5	63.6	63.4
Steam	25.8	23.5	36.4	36.6
Percent Carbon Burn-Off	58	41	21	40
Activated Char Properties				
Ultimate Analysis, wt %				
Ash	31.62	ND	23.15	28.68
Carbon	64.15	ND	72.17	66.91
Hydrogen	0.32	ND	0.37	0.34
Nitrogen	1.07	ND	1.43	1.18
Sulfur	1.59	ND	2.23	1.95
Oxygen	1.26	ND	0.65	0.94
Ball Pan Hardness Number	88.1	45.6	--	--
Apparent Density, g/ml	0.43	0.25	--	--
Sieve Analysis, mesh				
+6	--	--	--	--
-6+12	2.06	--	--	--
-12+20	10.89	36.57	20.6	20.59
-20+40	38.94	36.87	40.46	42.36
-40+60	35.80	19.63	26.90	26.95
-60+80	8.19	4.66	8.21	6.49
-80	4.12	2.27	3.83	3.61
Surface Area, m^2/g	825	--	611	8.15
Iodine Number	804	537	602	782

ND = Not determined.

Table 4, Part 3. SUMMARY OF RESULTS FROM CHAR ACTIVATION AND ADSORPTION TESTS

Test Number	2-29C	2-30A	2-40A
Char Source	P-2	P-2	P-2
Feed Char Composition (Dry), wt %			
Carbon	73.52	73.52	73.52
Sulfur	2.38	2.38	2.38
Ash	17.89	17.89	17.89
Activation Temperature, °F	1560	1560	1560
Duration of Activation, min	135	180	95
Activation Gas Composition, vol %			
Nitrogen	63.0	64.2	65.1
Steam	37.0	35.8	34.9
Percent Carbon Burn-Off	58	71	43
Activated Char Properties			
Ultimate Analysis, wt %			
Ash	36.99	45.62	23.61
Carbon	59.67	52.16	71.24
Hydrogen	0.23	0.29	0.31
Nitrogen	0.87	0.87	1.16
Sulfur	1.71	1.22	1.56
Oxygen	0.53	0	2.12
Ball Pan Hardness Number	--	--	75.9
Apparent Density, g/ml	--	--	0.47
Sieve Analysis, mesh			
+6	--	--	--
-6+12	--	--	--
-12+20	19.78	13.58	27.42
-20+40	40.14	40.55	41.07
-40+60	28.50	32.14	23.65
-60+80	7.60	8.75	5.78
-80	3.98	4.98	2.08
Surface Area, m^2/g	1000	1070	8.53
Iodine Number	832	896	763

The char in Test 2-11 was prepared from non-oxidized Illinois No. 6 coal. The batch of Illinois No. 6 coal without air oxidation that was fed to the 2-inch reactor sintered into one mass in the reactor. This mass was removed and ground and then steam activated at 1562°F. Its iodine number is comparable to those of the chars obtained from the PRU although it was not produced under the same fluidized-bed conditions.

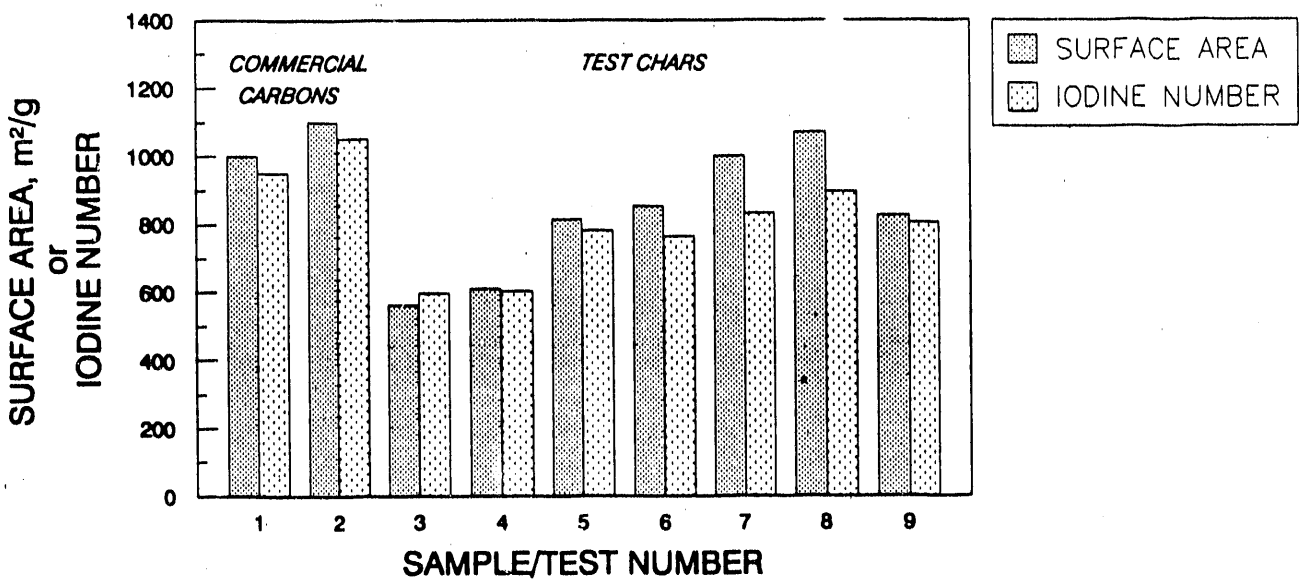
The difference due to air oxidation pretreatment of the coal was assessed with a Fisher assay of the liquids from the oxidized and non-oxidized coal samples. The values in Table 5 show the expected differences due to air oxidation. However, the char properties for steam activation should not be significantly affected.

Table 5. FISCHER ASSAY OF ILLINOIS NO. 6 COAL USED IN ADSORBENT STUDIES

Assay, wt %	Un-oxidized Coal as Char No. 1-50b	Oxidized As Char No. 2-28	Oxidized Overnight as Char No. 1-49	
Oil	15.1		9.6	1.6
Water	4.6		7.2	6.8
Residue	73.9		75.2	80.0
Gas + loss	6.4		8.0	11.6
Total	100.0		100.0	100.0
Oil Yield (gal/ton)	34.6		21.4	3.8
Water Yield (gal/ton)	11.0		17.3	16.2
Specific Gravity Oil at 60/60°F	1.046		1.068	1.023
API Gravity of Oil at 60°F	3.8		1.0	6.8

Iodine Numbers and Surface Area of Chars

The measured values of the iodine adsorption numbers and the surface areas of the prepared chars listed in Table 5 are presented in Figure 9. The reported values of a commercial adsorbent from Calgon Company and a typical bituminous coal-based adsorbent are included in the figure. The chars in this study compare favorably with the commercial adsorbents. The effect of steam activation on the iodine number and surface area of the chars is illustrated



SAMPLE NO.	DESCRIPTION
1	TYPICAL COMMERCIAL BITUMINOUS-BASED CARBON
2	CALGON TYPE OL
3	MG-6 CHAR - 100 MIN ACTIVATION
4	ILLINOIS NO. 6 CHAR - 45 MIN ACTIVATION
5	ILLINOIS NO. 6 CHAR - 90 MIN ACTIVATION
6	ILLINOIS NO. 6 CHAR - 95 MIN ACTIVATION
7	ILLINOIS NO. 6 CHAR - 135 MIN ACTIVATION
8	ILLINOIS NO. 6 CHAR - 180 MIN ACTIVATION
9	OXIDIZED ILLINOIS NO. 6 - 120 MIN ACTIVATION

SAGIN

Figure 9. SURFACE AREA AND IODINE NUMBERS OF ACTIVATED CARBONS

in Figure 10. Both the iodine number and the surface area increase with the activation time but the iodine number does not increase at the same rate as the surface area. This is probably due to increase in diameter of the small pores which contribute to the surface area but not the overall iodine uptake. This difference in rate is depicted in the plot in Figure 11 which shows the iodine number and surface area increasing with the carbon burnoff levels up to about 70%.

As the iodine numbers and surface area continue to increase with the increasing amount of carbon burnoff, there will be smaller amounts of carbon structure available for adsorptive capacity. Hence, the results were normalized by reporting the iodine uptake and the surface area per unit weight of char used in the activation. The iodine uptake and the surface area per gram of feed char is illustrated in Figure 12 as a function of carbon burnoff amount. It is seen that the net adsorptive values reach a maximum at 40% carbon burnoff.

Pore Size Distribution

The pore size distribution is important in adsorbents because it is related to the amount of surface area available for adsorbates of a specific size range. The pore size distributions of the micropores were determined for four selected chars in this study by the standard BET nitrogen adsorption isotherms. The adsorption isotherm of the Calgon commercial adsorbent was also evaluated. Figure 13 shows the commercial adsorbent to have a fairly even distribution of pores in the range of 10 to 500 Angstroms. The chars have a concentration of pores in the size range of 10 to 60 Angstroms. Increasing the extent of steam treatment increases the micropore volume and the percentage of larger pores as would be expected. For the adsorption of color bodies in effluent streams and high molecular weight organic materials, pores in the range of 20 to 500 Angstroms are considered to be best suited. Odor and low molecular weight organic species are best adsorbed with pores under 30 Angstroms in diameter. It appears that the chars may be well-suited for adsorption of low-molecular-weight organics.

Adsorption Performance With DCP and DMP

The char denoted 2-40a in Table 5 and the Calgon Type OL carbon were evaluated for the uptake of DCP and DMP. The characteristics of the sample

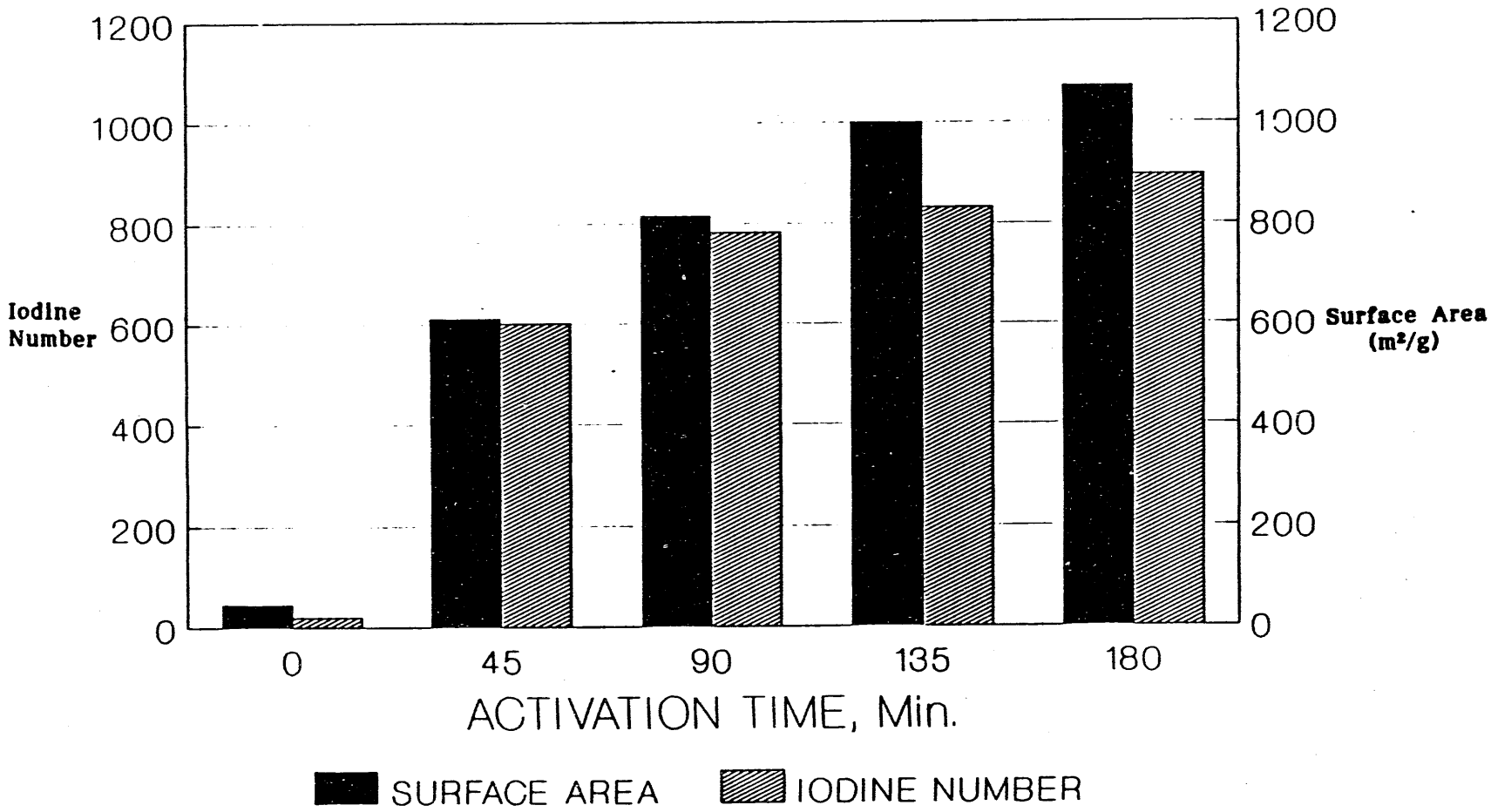


Figure 10. SURFACE AREA AND IODINE NUMBERS AS A FUNCTION OF ACTIVATION TIME

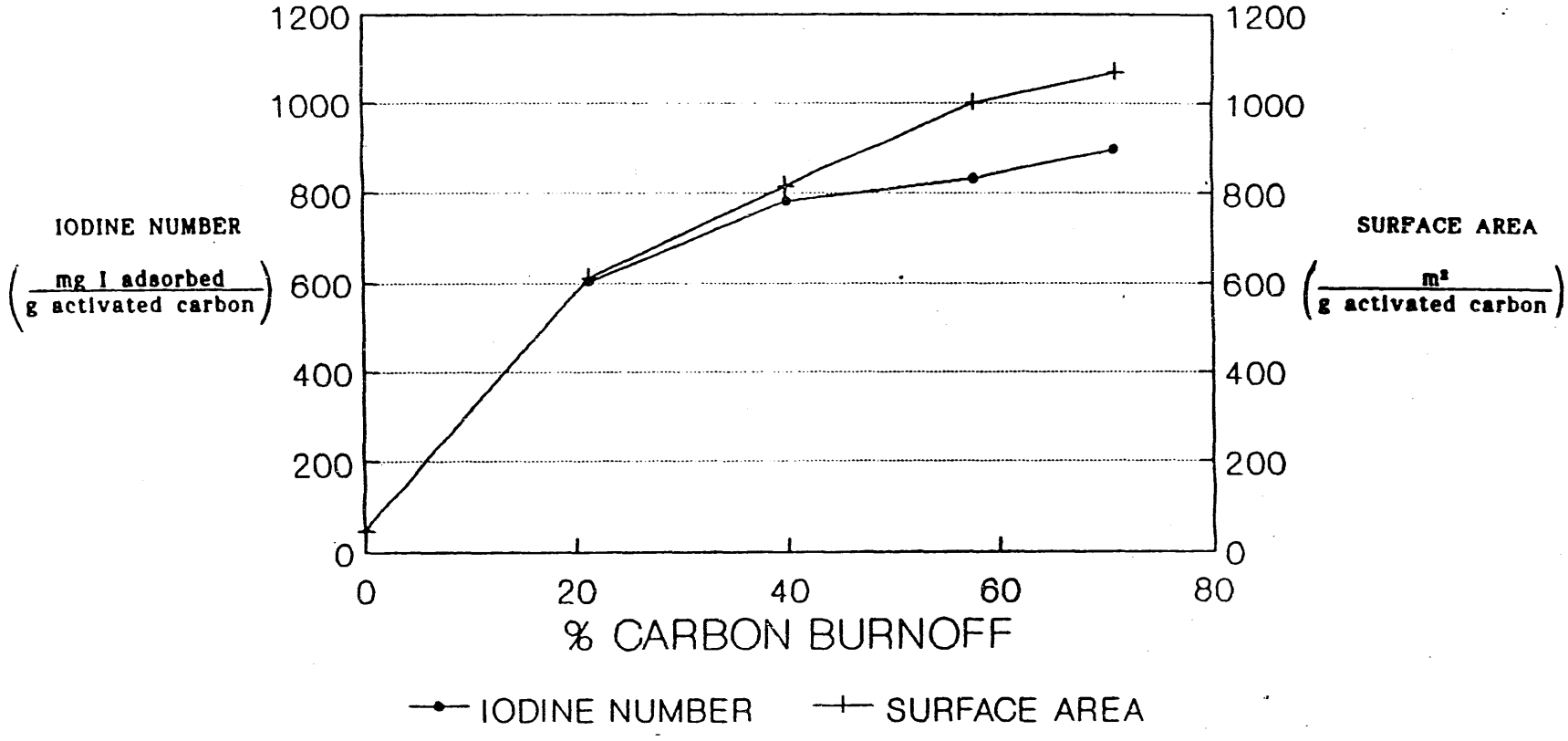
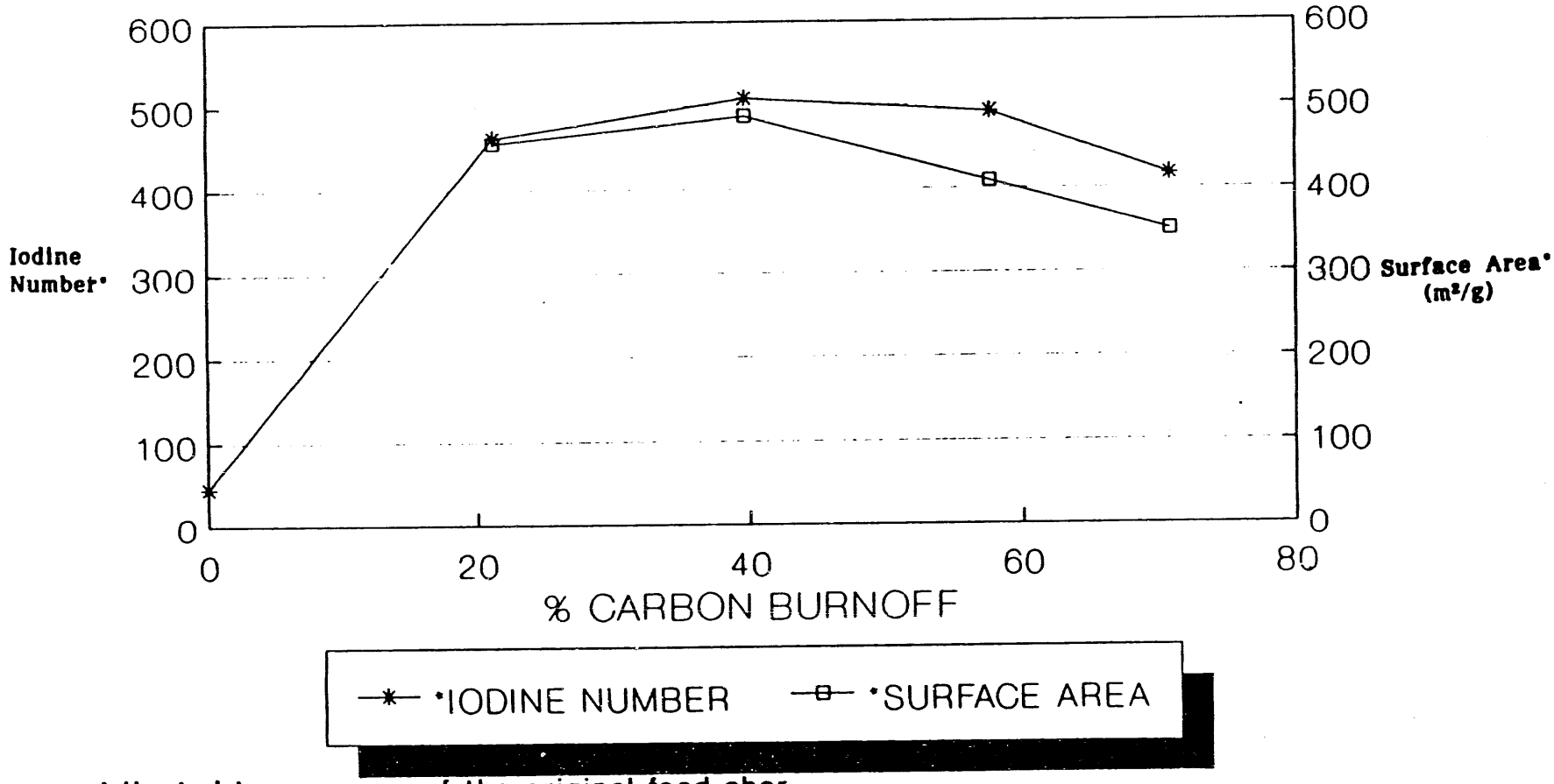


Figure 11. ADSORPTION PROPERTIES OF CHAR VERSUS CARBON BURN-OFF



* Adjusted to one gram of the original feed char.

Figure 12. CHAR ADSORPTION OPTIMIZATION FOR IODINE NUMBER AND SURFACE AREA

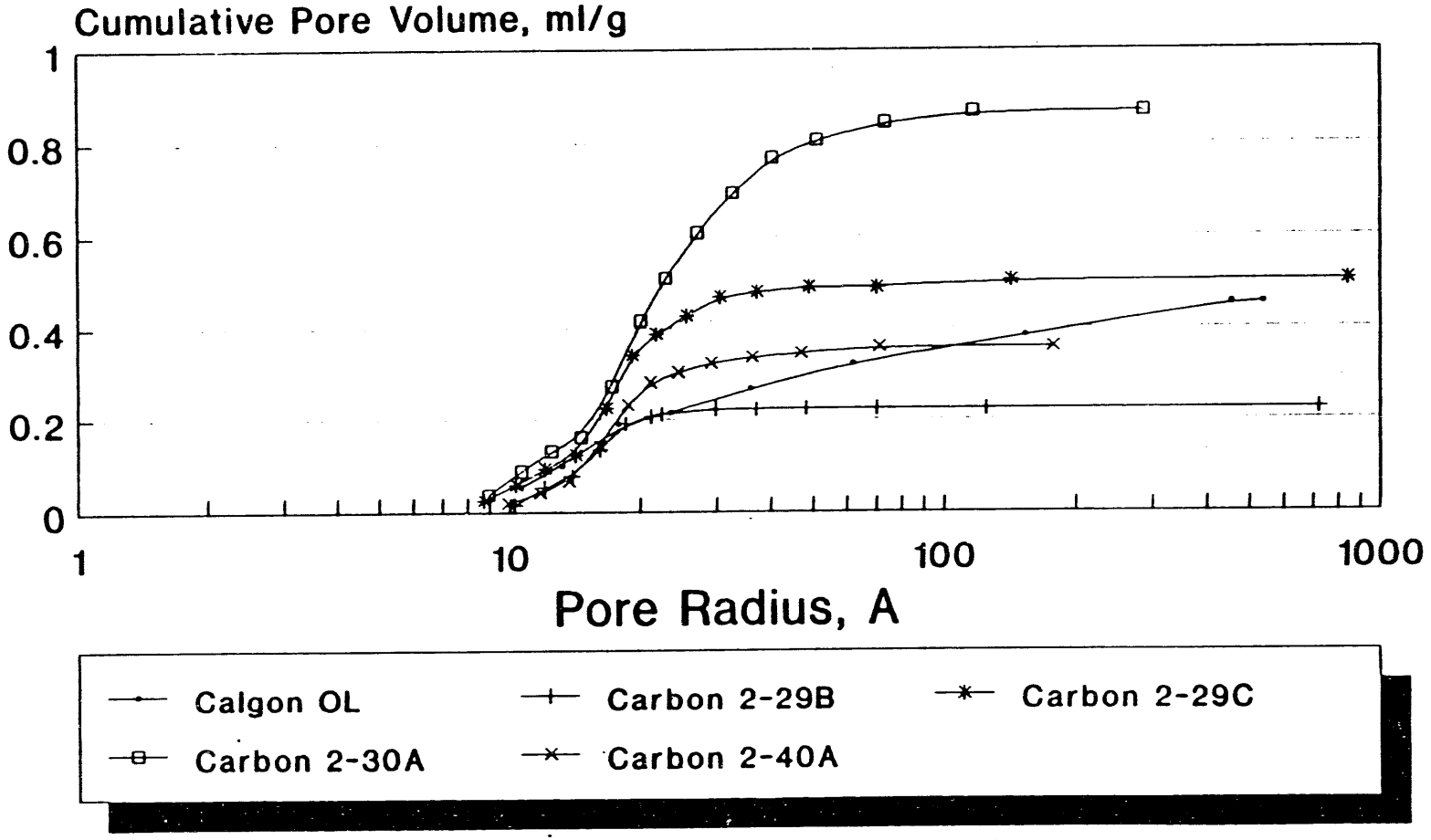


Figure 13. MICROPORE DISTRIBUTION OF SELECTED ACTIVATED CHARS AND CARBONS

char and the commercial adsorbent used in these tests are summarized in Table 6. The adsorption isotherm results are presented in Figures 14 and 15 for DCP and DMP adsorption, respectively.

Each carbon adsorbent showed similar isotherm slopes for DMP adsorption and the low slope of these lines indicate that the carbon adsorbents react similarly to changes in adsorbate concentrations. The DCP isotherm lines look quite different. At high concentrations, the Calgon adsorbent showed an equilibrium capacity for DCP about 1.5 times that of the char adsorbent. At lower concentrations of the adsorbate, the char adsorption capacity for DCP decreases significantly compared to the Calgon adsorbent. Depending on the adsorbate concentration, the Calgon adsorbent has an equilibrium concentration from 1.5 to 7.5 times the char adsorbent.

Single-solute batch kinetic tests were also conducted with both char and the Calgon activated carbon for both DCP and DMP adsorption. The measured uptake of these organic species versus time is shown in Figures 16 and 17. The char and the Calgon activated carbon behaved similarly in terms of the rate of uptake of both the DCP and DMP species with the rates leveling off after about 60 minutes. The char showed a higher uptake rate initially than did the Calgon adsorbent and overall a lower quantity adsorbed as measured in the equilibrium isotherms.

Table 6. ADSORBENTS COMPARED IN DCP AND DMP ISOTHERM TESTS

Adsorbent	Raw Material Source	Iodine Number	Surface Area, (m^2/g)	USS Mesh
Char 2-40a	Illinois No. 6	763	953	20 x 50
Calgon Type OL	Bituminous Coal	1050	1100	20 x 60

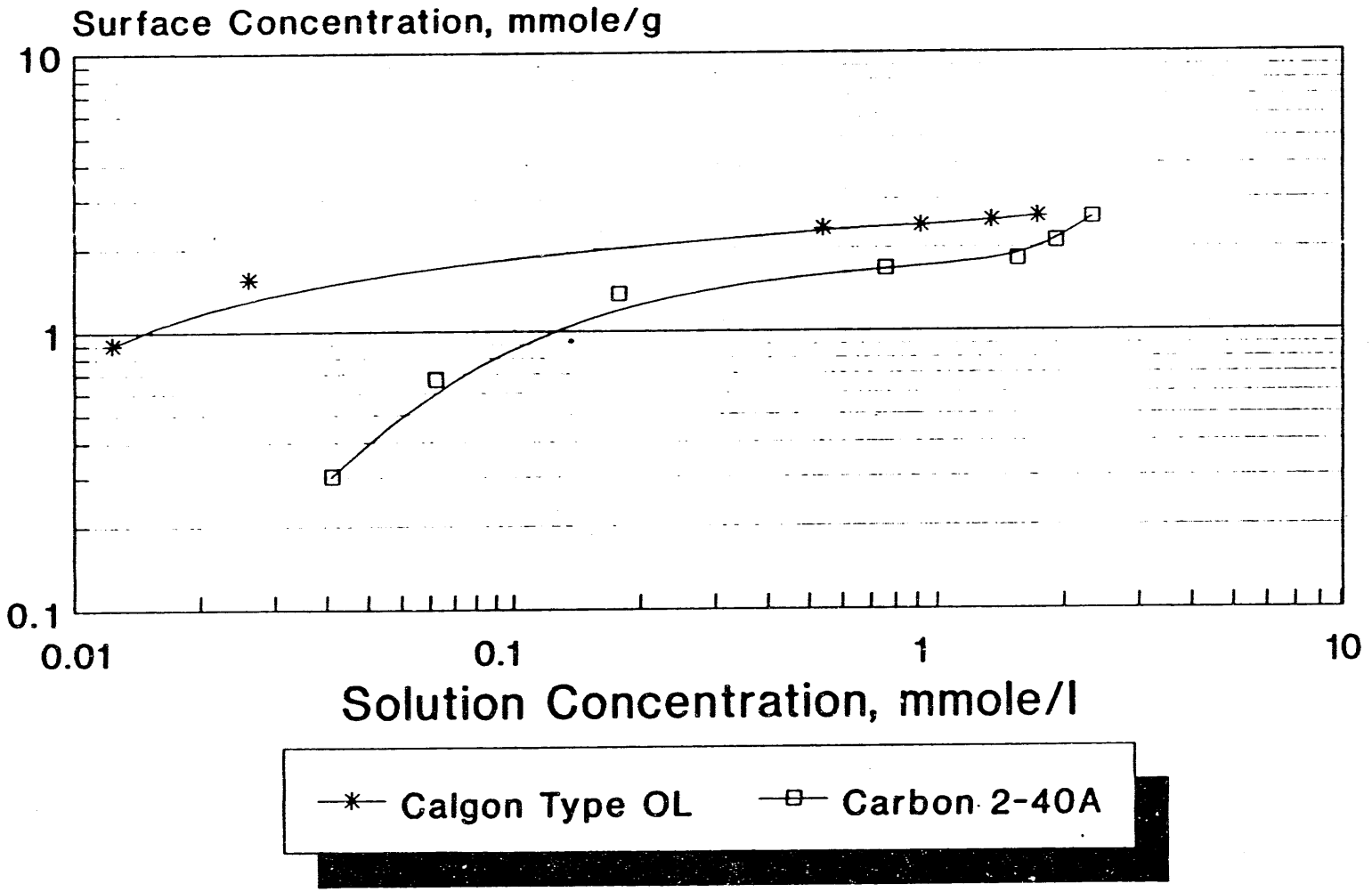


Figure 14. 3,5-DICHLOROPHENOL ISOTHERMS

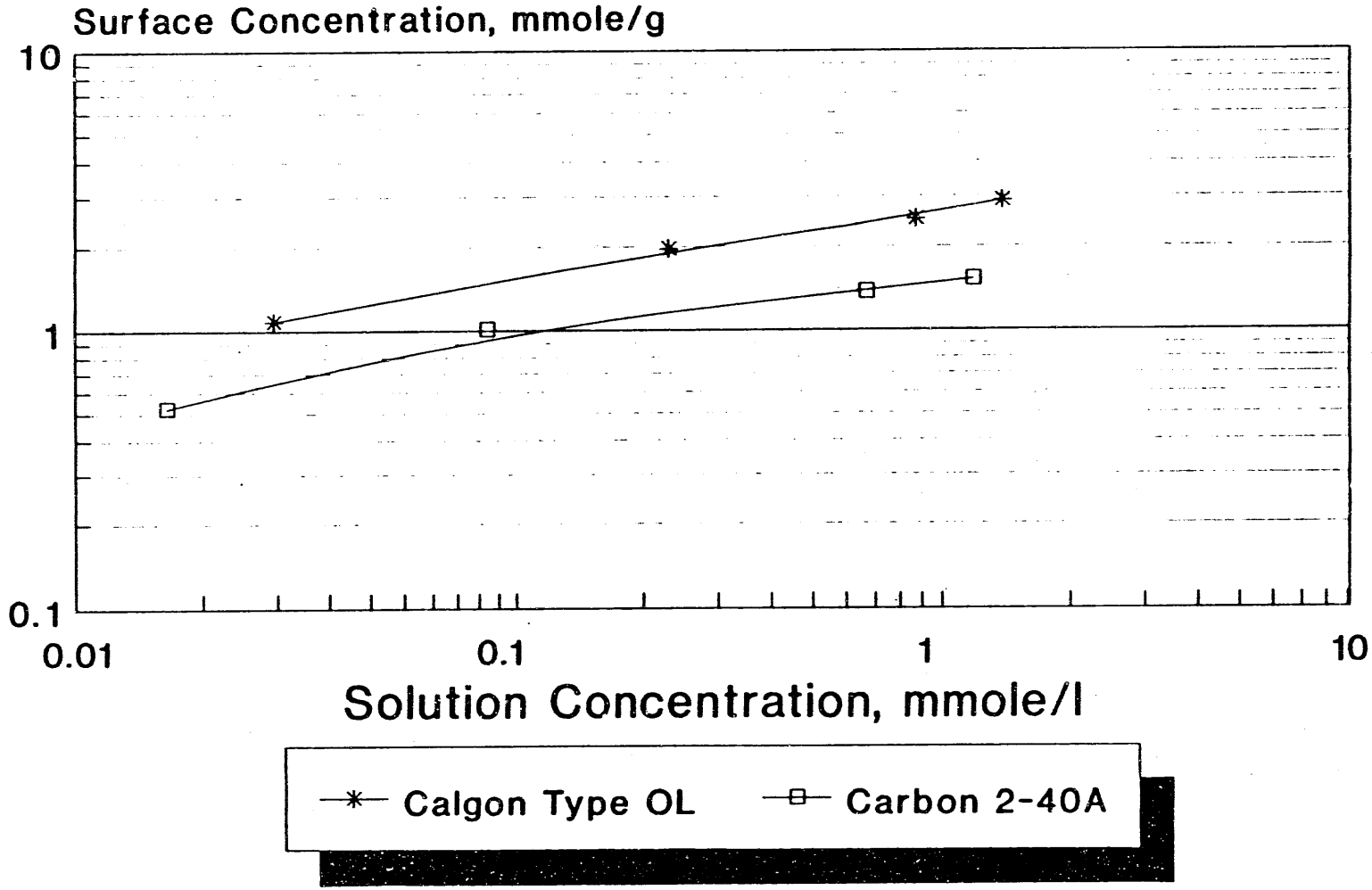


Figure 15. 3,5-DIMETHYLPHENOL ISOTHERMS

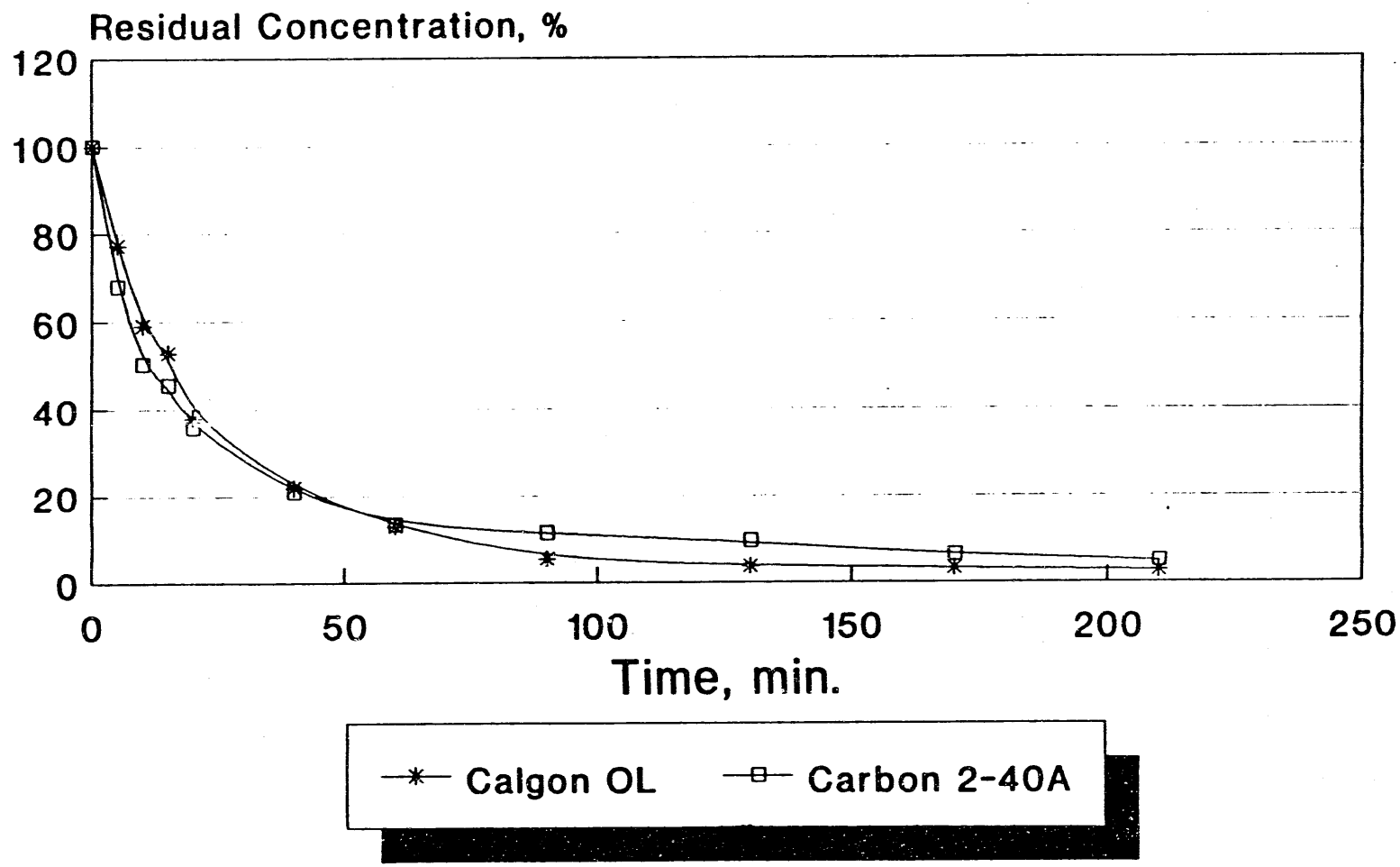


Figure 16. 3,5-DICHLOROPHENOL ADSORPTION RATES

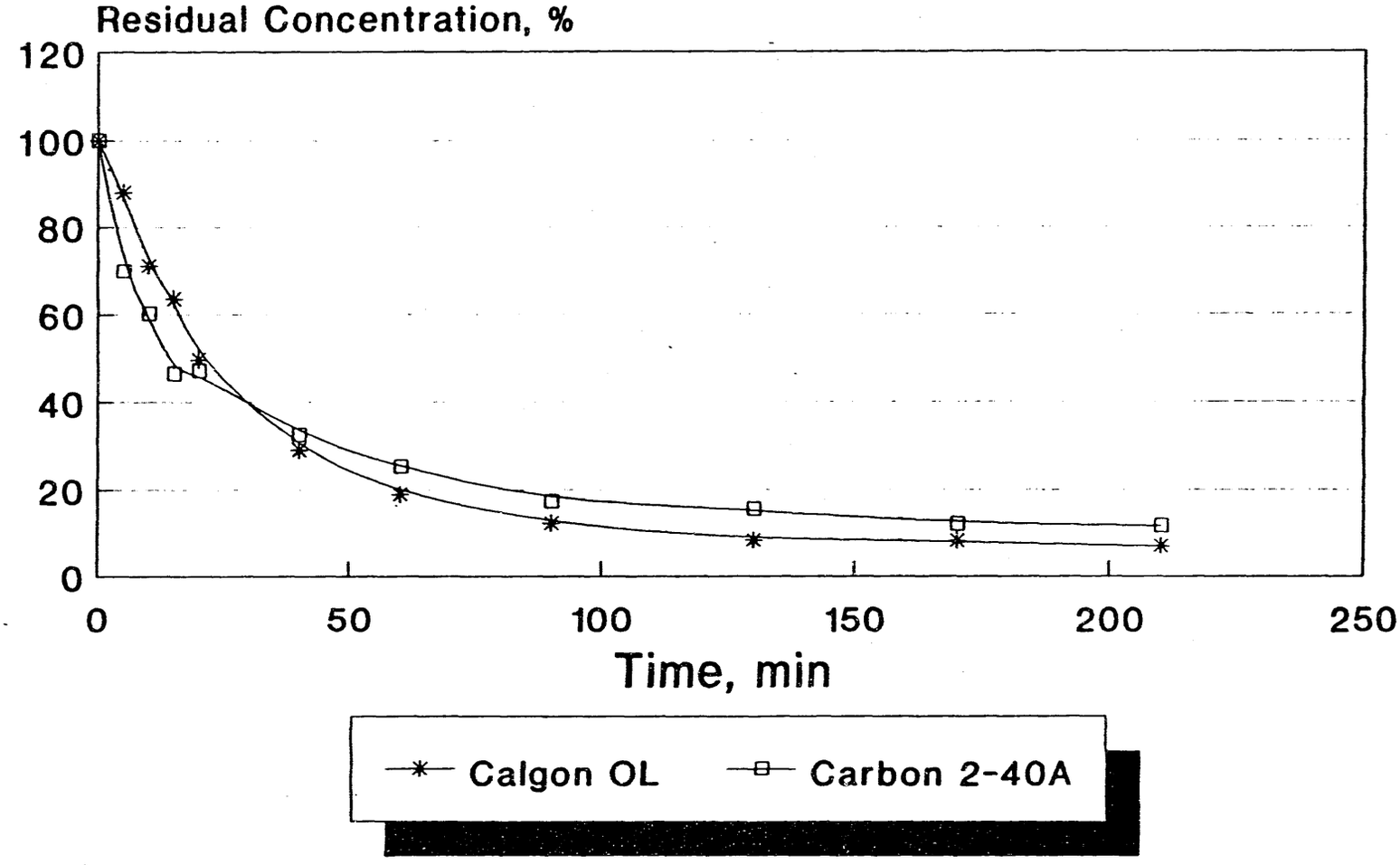


Figure 17. 3,5-DIMETHYLPHENOL ADSORPTION RATES

CONCLUSIONS

The three solid co-products made from mild gasification char with high value-added benefits were evaluated in Task 3 of this program. These co-products are a metallurgical form coke, an adsorbent char carbon, and a smokeless fuel.

The formation and testing for the form coke co-product involved an evaluation of its briquette strength and reactivity. An amount of coal equal to that of the char was used as the binder for form coke briquettes. The measured tensile strength and reactivity of the form coke sample briquettes were in the range of commercial coke, and development tests on a larger scale are recommended. The reaction rate of the form coke carbon with carbon dioxide at 1825°F was measured using the standard procedure specified by Bethlehem Steel Company. Various other tests and specifications have to be met to assess the potential success of form coke from mild gasification char, but the initial results are encouraging.

Three-inch-diameter briquettes were successfully made with their density and strength equal to a coke sample obtained from a steel company. About 1000 pounds of form coke were produced, using char from Task 4 PRU tests, in hot briquetting equipment at the research facility of a roll briquetting equipment manufacturer. However, the coal and char mixture temperature in the equipment could not be brought to the necessary value and, consequently, the briquettes were not of optimum strength after calcination due to expansion. Briquetting process variables need to be defined for each coal type and char product to tailor the processing to optimize physical and chemical properties necessary for form coke, foundry coke, or smokeless fuel.

A smokeless fuel briquette with limestone added to control sulfur can be made from mild gasification char in a simple manner. Test results have shown that briquettes with limestone have a heating value comparable to other solid fuels and the limestone can retain up to 88% of the sulfur during combustion in a simple bench-scale combustion test, almost all of it as a stable calcium sulfate. The production of smokeless fuel from mild gasification char, particularly from high sulfur coals, is recommended for further development both for indigenous and export markets.

Adsorbent char carbon from mild gasification represents another potential

co-product with a high probability of technical acceptance and a probable lower production cost compared to present commercial adsorbents. Char samples were prepared with a standard steam activation procedure and tested for a variety of pertinent property and performance values. These were compared with a commercially available adsorbent. After identifying optimum activation levels, we found that the mild gasification chars performed well. Such adsorbents may be better suited for use in some areas, such as the adsorption of low-molecular-weight substances, because of the smaller pore sizes measured in the char.

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