# ACTIVATED CARBON PRODUCTION FROM PETROLEUM COKE BY STEAM ACTIVATION AND STEAM-PHOSPHORIC ACID ACTIVATION

by

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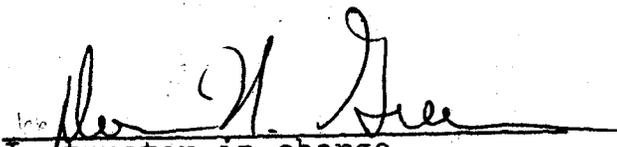
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SUMMARY

During the summer of 1966, representatives of the Kansas State Geological Survey, the City of El Dorado, Kansas, the Chemical and Petroleum Engineering Department of the University of Kansas, and the Economics Department of Wichita State University met to consider initiation of a program utilizing a new concept in industrial development. This concept involved using the area's raw materials, capital, technical capabilities and business knowledge to create a new industrial development. The proposed industrial development chosen was activated carbon production from petroleum coke produced at Skelly Oil Company's El Dorado Refinery.

The purpose of this work was to furnish answers to the following questions:

1. Can an activated carbon be made from the El Dorado Refinery's Petroleum coke?

2. If activated carbon is produced, how does its quality compare with that of commercially available activated carbon?

3. Can the activated carbon so produced be used for the specific commercial markets suggested in the economic study by Wichita State University, i.e., decolorizing carbon, water purification carbon, etc.?

It was decided to attempt to activate the petroleum coke by passing superheated steam through the coke bed. The reaction temperature range was approximately 800° C - 900° C. Isothermal activation tests were conducted

through the range to determine the optimum operating temperature. In a modified process, activation of the carbon was attempted by contacting the coke with phosphoric acid before introducing superheated steam.

Approximately 64 grams of 8-16 mesh petroleum were used for the test sample. Usually a steam flow rate of 9 ml/min, 18 ml/min, or 35 ml/min was employed during activation. The activation time was generally 0.5 hr., 1.5 hr., or 3 hrs.

The laboratory tests employed for evaluation of the treated coke as an activated carbon were the molasses test and the iodine test. The molasses test is used as an indicator for the decolorizing ability of the carbon. The iodine test is generally indicative of the carbon's ability to remove tastes and odors.

Data obtained from the molasses test were reported as per cent light transmittance through the molasses solution. Distilled water was used as the standard for calibration of the Beckman Model B Spectrophotometer. The ability of the carbon to function as a decolorizing agent was determined by comparing light transmittance values obtained from molasses solutions treated with commercial activated carbons to values obtained from the test coke samples. Light transmittance values could be duplicated within 0.5 per cent.

Data obtained from the iodine test were reported as per cent iodine removed. The per cent iodine removal data determined for the carbon test samples were compared to the results obtained using commercial carbons. A check on the reproducibility of the tests indicated that results could be duplicated within one percent or less.

The results of the molasses test indicate that the carbons produced have little or no decolorizing properties.

The two activation processes used, steam activation and phosphoric acid-steam activation produced carbons that adsorbed a maximum of 28% and 38% of the iodine stock solution respectively. Commercial carbons tested adsorbed 55% to 95% of the iodine stock solution.

It is concluded that activated carbon can be produced from petroleum coke. However, the quality of the activated carbon produced in these tests was poor. It is doubtful that a commercially competitive decolorizing carbon can be produced from the coke tested. It seems possible, however, that further modifications of the phosphoric acid-steam activation procedure could produce a low quality commercial grade carbon for use in water and/or gas purifications. An activation attempt by mixing phosphoric acid with the liquid feed to the Skelly Oil Company coking unit, carbonizing the liquid, and then steam activating might prove successful. Also, the addition of metallic chlorides to the petroleum liquid in the presence of phosphoric acid and/or sulfuric acid might improve the quality of the activated carbon produced.

It is believed that results obtained to this date indicate that the study should be continued at least until the proposed activation modifications have been attempted in the laboratory.

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CHAPTER I

INTRODUCTION

1.1 Origins of Thesis Study

During the summer of 1966, representatives of the Kansas State Geological Survey, the City of El Dorado, Kansas, the Chemical and Petroleum Engineering Department of The University of Kansas, and the Economics Department of Wichita State University met to consider initiation of a program utilizing a new concept in industrial development. This concept, named by the Kansas State Geological Survey as "Micro Planning," involves using an area's raw materials, capital, technical capabilities and business knowledge to create a new industrial development. The representatives accepted the project, and named it the El Dorado Project.

El Dorado city representatives initiated the project's first phase by selecting those mineral resources having highest probability of improved industrial development. The four most promising choices were studied in detail by the Kansas State Geological Survey. The evaluation criteria were marketability, durability, growth potential and production possibilities. The final choice was activated carbon production from petroleum coke produced at Skelly Oil Company's El Dorado refinery.

The project's second phase consisted of economic and engineering studies to determine the feasibility of developing a commercially competitive grade of activated carbon from the petroleum coke. The Mineral

Resources Section of the Kansas Geological Survey supplied research
financial grants to Wichita State University and to Kansas University.
These grants covered expenses for making a market cost-and-production
analysis of activated carbon, and for starting a research program to
determine the feasibility of making a commercially acceptable activated
carbon.

1.2 Purpose and Scope of Thesis Work

The purpose of this work was to furnish answers to the following
questions:

1. Can an activated carbon be made from the El Dorado Refinery's
    Petroleum coke?

2. If activated carbon is produced, how does its quality compare
    with that of commercially available activated carbon?

3. Can the activated carbon so produced be used for the specific
    commercial markets suggested in the economic study by Wichita
    State University, i.e., decolorizing carbon, water purification
    carbon, etc.?

1.3 Plan of Attack for Production and Evaluation of the Activated Petroleum Coke

Criteria for Production

An initial literature search conducted during September, 1966
disclosed very little published information pertaining directly to the
manufacture of activated carbon from petroleum coke. It was decided to
attempt activation of petroleum coke by methods generally similar to those
used in commercial productions of activated carbon. Procedural modifications

would be based upon information gained from the small amount of patent literature available concerning production of activated carbon from petroleum coke and from ideas developed during research.

The project's limited financial budget dictated use of existing equipment owned by the Department of Chemical and Petroleum Engineering, University of Kansas and by the Kansas Geological Survey.

Criteria for Testing

Laboratory tests for evaluation of the produced activated carbon had to meet the following criteria:

1. The tests used must cover the general range of properties significant for all uses of activated carbon.

2. The tests used must be currently recognized in industrial practice.

3. The tests must be simple and capable of being performed relatively inexpensively on available laboratory equipment.

Procedures and Tests Adopted

It was decided to try to activate the coke by using superheated steam (1450° - 1650°F.). Also, possible chemical treatments were envisioned. The laboratory evaluation tests to be employed were the molasses test and iodine test. Further discussion of testing procedure and manufacture will be found in Chapters III and IV.

CHAPTER II

REVIEW OF PREVIOUS WORK

2.1 Development of the Activated Carbon Industry

Modern commercial activated carbon is generally considered to
have developed from patents of R. Von Ostrejko issued in 1900 and 1901
(3,10). In these patents Ostrejko described a method for incorporating
metallic chlorides with a vegetable substance and carbonizing the mixture.
Also, he discussed a method for heating vegetable charcoal in bright red
heat while exposed to the oxidizing action of carbon dioxide. These
principles, mixing chemicals with the raw source material, carbonizing,
and/or the use of some oxidizing agent on the char are employed to some
degree by all activated carbon manufacturers today.

One of the earlier applications of activated carbon was in the
cane sugar industry where the carbon decolorized sugar liquors. However,
demand for decolorizing carbons was small and expansion of the activated
carbon industry was slow.

The most important stimulation given the activated carbon
industry occurred during World War I when on April 22, 1915, the Germans
launched a chlorine gas attack on the Allies. Considerable effort was
made to develop a material for use in protection against gas attacks. The
powdered activated carbons available were unsuitable for use in gas masks.
Activated carbon derived from coconut shells proved satisfactory because
of its resistance to abrasion and high potential adsorptive capacity (10).

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The great publicity given activated carbon during World War I stimulated research to find other areas of application for the material.

Currently, activated carbon markets include such fields as municipal and industrial water purification, dry cleaning, catalyst and catalyst carriers, gas masks, gas purification, gas separation, solvent recovery, corn and cane sugar, decolorization and pharmaceuticals (27,37).

The chief raw material sources for commercial activated carbon are pine wood, lignite, Michigan hardwood scrap, bituminous coal, wood pulp waste, blended petroleum hydrocarbon streams and coconut shells (37).

2.2 Literature Survey

Chaney, et al. (3), and Ray (26), described some of the necessary conditions for the production of activated carbon. They first suggested that carbonization of the raw material should be conducted at temperatures not exceeding 700° C. At temperatures above 700° C. hydro-cracking of the volatile material being liberated from the char was noted. These "cracked" hydrocarbons formed carbon deposits in the pore spaces of the char. This deposited carbon was highly resistant to activation attempts and also hindered further activation of the char. Such carbonization of the raw material does not always occur at or below 700° C. Thus, for any material, the temperatures where hydro-cracking of volatiles occurs generally establishes the upper carbonization temperature limit.

The second suggestion was that a higher degree of activation seemed to be attained by using an oxidizing agent for selectively oxidizing the carbonized material. Also, an excess of the oxidizing agent was proposed. Later, studies by Lewis and Metzner (17) on the activation of

fluidized birch chips by sulphur indicated that it was not always necessary for the oxidizing agent to be in excess. It is concluded that the necessary concentrations and amount of the oxidizing agent depend on exactly what materials are being used.

The third suggestion was that there is a correlation between the amount of hydrogen in the carbon and the degree of activation. Studies of activated carbon production from anthracite coal indicate the degree of activation increases as hydrogen content decreases.

Patents (5,11,23,24,25,39), pertaining to the manufacture of activated carbon from petroleum coke for the period from the 1930's to early 1940's, described various types of equipment and oxidizing agents to be used in the manufacture of activated petroleum coke. These patents suggested the use of steam and/or flue gas as the oxidizing agent.

A. L. Nugey (22) proposed a process of making activated petroleum coke by mixing the coke with a number of unspecified reagents and heating the mixture to temperatures of 300° F and 800° F for varying lengths of time. No tests of the efficiency of the carbon were reported except for two photo-micrographs of the carbon surface area.

More significant was the report of Fieldner, et al. (6). This report was a basic evaluation of activated carbon production from coal and other raw materials. The method consisted of one-hour treatment with 900° C superheated steam in an amount equaling twice the weight of the carbon. This attempt to activate petroleum coke did not prove to be successful.

During the 1950's various patents (1,2,38) were granted for making activated carbon from petroleum base by-products. Most methods started

with liquid petroleum by-products. They were carbonized sometimes in the presence of chemicals, and then treated with an oxidizing agent. Gaylor (9) described a patent granted Standard Oil Development Company whereby hot petroleum coke was mixed with acid sludge. The material was carbonized and later treated with steam. The resulting activated petroleum coke could be used for separation of both straight chain hydrocarbons and olefinic feed stocks.

CHAPTER III

PROCEDURE FOR PETROLEUM COKE ACTIVATION

3.1 General Principles Pertaining to the Activation of Carbon

Changes occurring while carbon is being activated are not currently well defined although the resulting increase in pore structure and surface area are well known.

It is often disconcerting to find that a step stated by literature to be essential in one process can be omitted in making an activated carbon from another source. It is known that the adsorption properties of an activated carbon vary with the source material and the activation technique employed.

The chief items governing the type of carbon produced are as follows:

1. Raw source material,

2. Carbonization with or without chemicals,

3. Oxidation.

A brief discussion of each of these items will follow.

Raw Source Material (10)

The type of raw material used for producing an activated carbon has a pronounced effect on the final characteristics of the resulting carbon. A strong, tough fibrous material such as coconut shells has

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proven highly effective for producing hard porous carbons needed for use
in gas masks. Such carbon can withstand mechanical abrasion when used
in fixed adsorption beds. Raw materials such as bone char have suitable
mineral composition for producing high quality decolorizing carbon.
Highly dense materials such as petroleum base by-products are usually
more suitable for gas and water purification than for use as decolorizers.
When wood pulp is mixed with minerals an adequate decolorizing carbon is
often produced. However, wood pulp usually has insufficient physical
strength to resist abrasion and thus usually is not used in fixed
adsorption beds.

Carbonization (4,10,20,21)

Activated carbons, cokes and chars are frequently referred to as
amorphous carbons. However, X-ray studies have shown that these
"amorphous" compounds actually are composed of sub-microscopic crystals
called "crystallites." X-ray studies indicate that the amorphous carbon
consists of flat plates wherein the carbon atoms are arranged in a hexa-
gonal lattice. Each carbon atom is held by covalent bonds to three other
carbon atoms, except for carbon atoms on the edge. Crystallites are
formed by two or more of these flat plates stacked above each other. In
addition to differences in crystal size, carbon crystallites and graphite
crystals differ in the following manner:

1. The plates of a graphite crystal are closer together than
   in the crystallites.
2. The stacking of plates follows a definite crystalline pattern
   in graphite but not in carbon crystallites.

The size of the crystallites is influenced by the temperature of carbonization. The mechanism of crystallite formation may be one of the following:

1. During carbonization the raw organic material may split into fragments and reform in a thermo-stable aromatic structure.

2. It is also possible that the hexagonal plate lattice grows gradually at the expense of the raw material. The transformation is seldom complete. Thus, remaining residual hydrocarbon chains and rings remain on the lattice edges.

If an oxidizing agent is used after carbonization, many of these hydrocarbon chains are removed leaving more pore space in the carbon mass.

In some processes mineral salts are added to the raw material and then carbonized. The addition of the mineral salts may have two effects:

1. The salts tend to provide a skeleton on which the carbon is deposited.

2. The mineral salts help spread the crystallites thus creating more pores in the carbon mass.

Often the mineral salts are washed-out after carbonization, thus leaving additional pore space in the carbon.

Oxidation (3,10,26)

An oxidizing agent is often employed during or after the carbonization step.

The type of adsorptive powers resulting from activation by oxidation are determined by the following:

1. Chemical nature and concentration of the oxidizing agent.

2. Temperature of reaction.

3. Length of time for activation.

4. Amount of mineral ingredients in the carbon.

Today the oxidizing agents most commonly employed industrially for the carbonization processes are steam and flue gases. They are used because the endothermic reaction caused by these gases is more easily controlled than exothermic reactions.

The oxidizing agent increases the surface area of the carbon by forming carbon dioxide and carbon monoxide from the carbon surface and also by removing the hydrocarbon chains formed on the crystallites during the carbonization stage. The various minerals present in the char influence the optimum reaction temperature and also the initial carbon pore space that can be exposed to the oxident.

Summary

It may be concluded that though many patents have expired and can be used freely, making actual use of a patent usually requires major changes to obtain practical results. The activated carbon industry as it now exists has been developed largely through trial and error. The secrecy with which the various manufacturers protect their processes, the complexity of their procedures and the lack of real understanding of the mechanisms involved in the production of various types of activated carbon create major difficulties for inexperienced persons attempting production of a commercially satisfactory activated carbon following study of literature and patents.

3.2 Preparation of Raw Coke for Activation

Petroleum coke obtained from the Skelly Oil Company El Dorado Refinery's coking unit during the latter part of September, 1966, was used in this project. A portion of the coke submitted was crushed and screened. That portion of the crushed coke having particle sizes between 8 - 16 mesh coke was obtained. The reason for using 8-16 mesh coke particles was purely arbitrary, being based on suggestions contained in some of the patents.

3.3 General Description of the Activation

Process Used

It was decided to attempt to activate the petroleum coke by passing superheated steam through the coke bed. The steam-carbon reaction temperature range has been cited by Hassler (10) as approximately 800° C - 900° C. Isothermal activation tests were conducted through the range to determine the optimum operating temperature. The reasons for choosing a steam activation process were as follows:

1. Steam activation is one of the primary industrial methods for making activated carbon.

2. The steam-carbon reaction is endothermic and is generally easier to control than an exothermic reaction such as that produced by using air as the oxidizing agent.

3. If a laboratory steam activation process were successful, and the process commercially feasible, then steam to be used for the commercial operation would be readily available at the El Dorado Refinery.

4. The fire safety hazard would be minimized with steam as the
    oxidizing agent as compared to air or sulfur.

In a modification of the process, activation of the carbon was attempted by contacting the coke with phosphoric acid before introducing superheated steam. It was decided to use phosphoric acid because it is one of the few chemicals that will assist in activation after carbonization has occurred. A general discussion of these two processes follows.

Steam Activation

Figure 1 is a flow diagram of the steam activation process. Gaseous nitrogen from cylinder (A) supplied the driving force to move distilled water from storage tank (B) into boiler (C). A pressure of approximately 25 psig. was maintained on the surge tank by means of the nitrogen cylinder's pressure regulator. The boiler produced steam at a maximum working pressure of 20 psig. and a rate of approximately 40 cc/min. Steam from the boiler travelled to the superheater section (D) located in the Harper Electric Furnace (E). The steam was superheated to the desired temperature and passed to the reactor tube (F). Steam pressure in the reactor tube was 1.0 ± 0.5 psig. The exit steam temperature was monitored (G) and the electric furnace transformer (H) was manually turned off and on maintaining a constant exit steam temperature from the reactor within ± 5 F. The steam flow rate to the reactor was hand-controlled by adjusting a 1/4 inch stainless steel needle valve (1). The exhaust steam passed to a condenser consisting of a 12 ft. coil of 1/4 in. diameter copper tubing immersed in a water-filled tank (I). The steam condensed and collected in a water trap (J). Uncondensed gases leaving the water trap passed to the wet test meter (K) where they were measured.

The activation time for the process was varied from 0.5 to three hours.

Phosphoric Acid and Steam Activation

The process was essentially the same as previously described except that coke was treated with phosphoric acid prior to the steam activation step.

A more detailed description of the equipment and process operation may be found in sections 3.4 and 3.5.

3.4 Description of Equipment and Specifications

Most of the equipment description and specifications are shown on Table 1. Also, Exhibits 1 through 10 are photographs of different sections of the process flow system.

The following discussions supplement Table 1 giving descriptions of the equipment and its usage.

Exit Steam Thermocouple Probe (Exhibit 1)

The thermocouple probe was made from 20 gauge alumel chromel wire, 21 inch in length. Because of the corrosive gaseous atmosphere leaving the reaction tube, the thermocouple wires were protected with ceramic insulators. The thermocouple junction was covered with Saureisen Cement. The thermocouple probe and recorder were standardized by placing the probe in the Harper Electric Furnace, (Exhibits 8,9,10), and simultaneously comparing its reading with temperature values obtained from the furnace probe and a Honeywell-Rubicon potentiometer. The readings agreed to within $\pm$ 10° F. throughout the 1350-1750° F. range employed. Consequently,

the constructed thermocouple probe and its recorder were considered to be functioning properly.

Thermocouple Steam Flow Rate Control Assembly (Exhibit 2)

This piece of stainless steel piping assembly had three main functions:

1. Carry exhaust gas and serve as a steam delivery pipe to the condenser.

2. Control flow rate of steam to the reactor.

3. Serve as the housing for the thermocouple probe which measures the temperature of steam leaving the reactor.

The overall length of the thermocouple and steam flow rate assembly was 19 inches. The thermocouple probe, which held the assembly by threaded connections, ran longitudinally down the length of the pipe. The centering of the probe was accomplished by a 50 mesh stainless steel screen inside the one-inch threaded coupling on the inlet end of the assembly. A hole punched in the center of the screen permitted passage of the thermocouple probe. The probe extended approximately 2 inches beyond the piping assembly. Thus, the tip of the probe extended into the reaction tube and was immediately adjacent to the exit end of the petroleum coke charge.

The end of the piping assembly extended approximately 4 inches outside the furnace. Therefore, the location of the steam flow rate control valve was accessible for hand control operation.

Connection of the Superheater Section, Reaction Tube, Thermocouple - Steam Flow Rate Control Assembly (Exhibit 5)

It was decided to use threaded fittings for connections between the superheater section, reaction tube, and thermocouple-steam flow rate control assembly. Threaded fittings offered a relatively easy way of installing and removing the reaction tube from the assembly when loading and unloading the coke test sample. Lubricant for the pipe threads was made from a mixture of molasses and flake graphite. Upon heating, the molasses burned away leaving the graphite in place.

3.5 Details of Activation Process

Equipment Assembly:

Usually a 64.1 ± 0.1 g. charge of the 8-16 mesh petroleum coke was placed in the reaction tube (Exhibit 3) and held in position by 50 mesh stainless steel screen supports placed at each end of the coke charge. A 2 inch void space was left at the end of the reactor tube to house the junction of the exit-steam thermocouple probe. The loaded reactor tube was then coupled to the steam superheater section. The steam flow rate control assembly (Exhibit 2) was then connected to the reaction tube exit.

The superheater, reactor, and steam flow rate control assembly so connected, were placed in the Harper Electric Furnace so that approximately 4 inches of the steam flow rate control assembly extended beyond the furnace. A 1/2 inch diameter insulated copper tube was connected between the Chromalox Boiler steam exit and the superheater inlet. A 1/4 inch diameter copper condensing coil was connected to the steam flow rate control valve (1). The condensate accumulator (J) and the wet test meter

(K) were then connected to the steam condenser outlet. The furnace opening was then sealed by the use of fire brick to help reduce heat loss. Exhibit 9 shows the assembled equipment.

Production of Treated Coke by Steam Activation

With the completion of the equipment assembly, the power transformer (H) for the Harper Electric Furnace was turned on. The temperature recorder controller (L) was set at the desired temperature. The activation temperature used for each sample run was controlled ($\pm$ 5°) at a selected point within the temperature range 1450 - 1650° F. Approximately 4 hours were required to bring the furnace to the desired temperature.

A nitrogen gas purge was maintained on the coke, while raising the furnace to operating temperature. This was done to insure against fires or explosions.

The procedure used was as follows:

1. The copper tubing from the nitrogen cylinder to the water surge tank was disconnected at valve #2.

2. A 1/4 inch diameter copper tube was connected between 1/4 inch valves #2 and #3.

3. Valves 1, 2, and 3 were opened.

4. Valve 4 was closed.

5. The end of the cooling coil was removed from the condensate accumulator.

6. The nitrogen cylinder pressure regulator was set for a 1 psig. discharge pressure.

The purge was continued until the desired reaction temperature was attained as indicated by the recorder measuring exit gas temperature (G) from the reactor. The boiler heating and the nitrogen purge were started simultaneously. With valve 4 closed, the boiler pressure was allowed to increase to its 20 psig. working pressure. No steam was passed over the sample until exit purge gas reached the control operating temperature. Steam was then admitted and the activation of the coke was begun.

Steam activation of the coke proceeded as follows:

1. The nitrogen pressure regulator was turned off.

2. The 1/4 inch diameter copper tubing connecting valves 2 and 3 was removed.

3. Valve 3 was closed.

4. The 1/4 inch diameter copper tubing connecting the water surge tank to the nitrogen cylinder was reconnected to valve 2.

5. Valves 1, 2, and 5 were checked for open position.

6. Valve 6 and 7 were checked for closed position.

7. The nitrogen pressure regulator was set for 25 psig. discharge pressure to the water surge tank (B).

8. Valve 4 was opened completely permitting steam to flow to the superheater and reactor.

9. The steam flow rate was controlled by adjusting valve 1.

10. The exit steam flow rate was determined by measuring the flow rate of condensed steam from the reactor. A 100 ml. graduated cylinder and a stop watch were used for this measurement.

Flow rates were usually set at one of three rates; 9, 18, 35 ml condensate/min. ± 0.5 ml.

11. When the flow rate had been established the condenser coil was again connected to the condensate accumulator and the gas flow rate was then metered.

Steam was passed over the sample for a selected time, usually 0.5, 1.5, or 3 hours. During this period, the exit steam temperature was monitored and the electric power input to the furnace was hand controlled to maintain a constant exit steam temperature. Hand control was necessary because the furnace temperature controller was not operating properly. The temperature differential between the furnace temperature and the exit steam temperature varied between 20 - 30° F. It was therefore considered that the reaction was being conducted essentially isothermally, i.e., steam inlet and exit temperature to the reactor were approximately the same.

With completion of the run, the following shutdown procedure was used:

1. Power to the boiler and the furnace was shut off.

2. Valve 3 was opened and the steam vented to the atmosphere.

3. The nitrogen cylinder was closed.

4. The total volume of gas indicated on the wet test meter was recorded.

5. The volume of water collected in the condensate accumulator was measured.

6. The furnace was allowed to cool for approximately 12 - 14 hours.

Production of Treated Coke by Phosphoric Acid and Steam Activation

This process for production of treated petroleum coke is essentially the same as previously described with these modifications. Concentrated phosphoric acid (85% by weight) was mixed with the petroleum coke sample in sufficient quantity (approximately 10 ml H_3PO_4 per 64.1 g. coke) to wet the coke surface. The phosphoric acid-coke mixture was placed in the reactor and the equipment assembled. The equipment assembly and steam activation procedure were then conducted as described in Section 3.5.

Collection of Treated Coke

The reaction tube and superheater were removed from the furnace when the temperature had dropped to about 200 - 300° F. The reaction tube was disconnected from the superheater. The treated coke was removed from the reaction, weighed, and sealed in a small 4 ounce jar.

3.6 Problems with Process Flow Equipment

Some difficulties were experienced with the process flow. A discussion of these problems follows.

Reactor Tube

The reactor tube was made from 1 inch O.D. Type 304 stainless steel pipe. The reaction temperatures (1450-1650° F) and the gaseous atmosphere existing in the tube caused severe corrosion of the tube's interior. Addition of phosphoric acid hastened the deterioration of the reactor. Pieces of iron oxide dispersed in the treated coke. These iron particles were removed from the coke by use of a magnet and screening. If further tests are conducted, it is suggested that the reactor be made of ceramic or some other material which would resist corrosion.

Steam Flow Rate Measurement

The steam flow rate was measured on the exit end of the reactor and therefore was not the true rate of steam delivered to the reactor. However, by accounting for the steam used in the reaction, it was found that the variation between the two rates was about 1.0 ml/min. This variation is considered insignificant.

Location of the Reactor Tube

The physical dimensions of the furnace interior required that the reactor tube be placed horizontally. Consequently, because of carbon shrinkage during activation, steam channeling occurred. It is not known what effect, if any, the channeling had on the absorptive properties of the resulting carbon.

Measurement of the Reaction Temperature

It was desired to maintain an essentially isothermal reaction during the activation process. The reactor exit steam temperature was monitored directly. The inlet steam temperature was not measured. However, it was noted that the difference in temperature between the furnace interior and the exit steam was about 20 - 30° F. It was concluded that the inlet and exit steam temperatures did not vary enough to offer any major problem in optimizing the reaction temperature.

CHAPTER IV

TREATED COKE EVALUATION TESTS

The selections of laboratory tests to evaluate the degree of carbon activation attained were based on the following criteria:

1. Recognition by industry.

2. Tests showing the general adsorptive properties of the carbon.

3. Inexpensive.

4. Capable with available laboratory equipment.

The analytical procedures selected were the molasses and the iodine tests. In this study the molasses and iodine test values of the treated coke were compared directly with values obtained using commercial activated carbons. No attempt was made to measure the surface area of the carbon because the required equipment was not available and would be expensive to obtain.

4.1 Discussion of the Molasses Test (10,18)

The molasses test is probably one of the most widely used industrial tests for evaluating carbons. This procedure was at one time the only control test used to evaluate many of the commercial carbons. It was generally assumed that a satisfactory molasses relative efficiency value (M-RE) indicated that all adsorptive powers had been uniformly

developed. It is now recognized that some deviation in the activation process can alter various adsorptive powers of the carbon and not be disclosed by M-RE test data.

In its primary use, the molasses test indicates the decolorizing properties of an activated carbon. The test is much used in the sugar industry because it gives a good index of results obtainable in decolorization of sugar liquors. The molasses test has, however, some distinct limitations according to the source of molasses used. The test results obtained when using one molasses stock will differ from the results obtained with another molasses. Therefore, it is necessary to compare the molasses value of a test carbon with the molasses value of a reference carbon retained as a standard. The procedure used in conducting the molasses test is described in Appendix II-B.

4.2 Discussion of Iodine Test (10,13,18)

The iodine test appears more indicative of a carbon's ability to remove flavors and odors than of its decolorizing ability. The test uses standard chemical solutions. Test results are therefore chemically reproducible. This test is also used extensively in industry as a quality control test. The test procedure and evaluation of the iodine test may be found in Appendix II-A.

The use of the iodine test and the molasses test tend to give a composite evaluation of the carbon's adsorptive qualities. The two tests complement each other because each evaluates different properties of the carbon. The molasses test give a qualitative indication of the macropore

structure of the carbon (pore sizes 100 angstroms or larger) while the iodine test offers a qualitative idea of micropore structure (100 angstroms or less). However, there is actually an overlapping of adsorptive ranges because the molasses test is influenced by pore sizes as small as 28 angstroms.

CHAPTER V

TEST RESULTS AND DISCUSSION

5.1 Results

Iodine Test

The results of the iodine test are listed in Tables 2 and 3.
Figures 2, 3, 4, and 5 represent various correlations of the data obtained.
Figure 2 is a comparison of the effect various steam flow rates have on
the degree of carbon activation as indicated by the iodine test. Figures
3 and 4 show the variation of iodine adsorption with reaction temperature.
Figure 5 is a graph comparing iodine adsorption results obtained from two
different carbon activation procedures. Iodine adsorption values obtained
from commercial carbons are plotted for comparison with the test samples.

Molasses Test

Data for the molasses test are tabulated in Table 4. Figures 6,
7, and 8 represent a correlation between the carbon's decolorizing ability
(recorded in per cent light transmittance) and hours of steam activation.
Distilled water was used as the light transmittance standard. Commercial
carbons were also tested for comparison purposes.

Coke Analysis

Analyses of the raw and treated coke for carbon-hydrogen ratio, ash content and per cent volatiles were made by the Skelly Oil Company (7). The results may be found in Appendix I, Exhibits 12 and 13. Also, the Kansas State Geological Survey conducted a spectro-graphic analysis of the raw coke giving a qualitative analysis of mineral content. These results are presented in Appendix I, Exhibit 14.

Reactor Exit Gas Analysis

An analysis of the reactor exit gas for sample 22 was made. The procedure and results of the analysis and material balance for Run 22 are listed in Appendix II.

5.2 Discussion

Iodine Test

A check on the reproducibility of results for the iodine adsorption test was made. Iodine adsorption results were duplicated with a maximum error of $\pm$ 0.15 g/l for a given sample. Test results were reported to the nearest per cent. Tables 1 and 2 show the iodine test data. Iodine test results are given in two tables because the concentration of the test iodine stock solution was not duplicated when the original stock solution became depleted. Test samples 1-12 were run using a 21.02 g/l iodine stock solution. Samples 13-22 were run using a 24.46 g/l iodine stock solution. Test samples 7, 8, 10 and 12 were re-tested using the 24.46 g/l iodine stock solution. Comparison results for samples 7, 8,

10 and 12 indicate that the above variations in concentration of iodine stock solution did not significantly alter the concentration of iodine adsorbed.

The difference in concentration of the iodine stock solution occurred because the stock solution used for test samples 1 through 12 had deteriorated slightly during two months standing prior to usage. The stock solution used for samples 13 through 22 was prepared and used immediately.

Figures 3 and 4 indicate that the optimum reaction temperature for steam activation is in the range of 1500-1550° F.

An inspection of Figure 2 indicates that the variation of steam flow rate has relatively little effect on the coke's iodine adsorption capacity. However, test results obtained indicate that at constant activation time and temperature the amount of product recovery is reduced as flow rate increases. (Refer to Table 5.) The above observations agree with the results obtained by Fieldner, et al. (6).

Data obtained regarding the degree of the activation and the amount of coke recovered for various flow rates tend to indicate that the steam-carbon reaction is occurring primarily on the coke surface. It appears that at least part of the controlling reaction mechanism for carbon activation is diffusion of the oxident into and out of the pore lattice of the carbon.

Because the major portion of the adsorptive capacity of an activated carbon is attributed primarily to the surface area of the micropore lattice system it is important that the oxidizing agents used for activation be able to penetrate the carbon and consequently increase this surface area.

It is known that petroleum coke is a very dense material when compared to other sources used for producing activated carbon (6). Since the experimental data obtained indicate little development of the micropore system, further activation attempts should be oriented towards enlargement of this system. Phosphoric acid was used for this attempt. Figure 5 shows that the phosphoric acid-steam activation process developed a higher degree of activation than the steam activation process.

Molasses Test

A check on the reproducibility of test results indicated that transmittance test data could be duplicated within $\pm$ 0.5%. Figures 6, 7, and 8 represent the values obtained at varied reaction temperatures. Comparison of transmittance values for treated and untreated coke samples show little improvement (Table 4). Carbon samples which were only boiled in phosphoric acid with no subsequent steam treatment showed higher light transmittance values than carbons treated by either the phosphoric acid-steam or steam activation process. Sample A (Table 4) produced a reading of 18% transmittance as compared with about 13-14% for carbon activated by use of steam, and by combined phosphoric acid steam.

Coke Analysis and Reactor Exit Gas Analysis

The analysis of the raw and treated coke for hydrogen-carbon content indicate that some hydrogen was removed during attempts at activation. Chaney (3) and Ray (26) stated that activation of the raw material increases as the hydrogen-carbon ratio decreases. Data for Sample 1 of Exhibit 12 indicate the per cent carbon and hydrogen existing in the raw

coke test sample. Samples 7 and 21 indicate the per cent hydrogen remaining after treatment with steam and phosphoric acid-steam respectively. The phosphoric acid-steam treatment removed more hydrogen than the steam activation attempt. These results and the statements of Chaney and Ray would indicate that the phosphoric acid-steam activation attained a higher degree of coke activation than the steam activation attempt. This observation is further verified by the iodine test results, Figure 5 and Table 2.

An analysis of the reactor exit gas for Sample 22 (Appendix II-C) was made. A comparison of the resulting $CO-CO_2$ ratio is in general agreement with results obtained by May et al. (19).

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

The laboratory tests show that an activated carbon can be made from petroleum coke. In these tests 30-50 per cent activated carbon recovery could be obtained. However, the quality of the carbon was poor. Commercial carbons tested adsorbed approximately 55 to 95 per cent of the iodine stock solution. The two activation processes used, steam activation and phosphoric acid-steam activation, produced carbons that adsorbed a maximum of 28 and 38 per cent of the iodine stock solution respectively. As stated in Chapter 4, the iodine test gives an indication of a carbon's ability to remove taste and odors.

The results of the molasses test indicate that the carbons produced have little or no ability to function as decolorizing agents. Although the test values recorded did in some instance equal values for commercial carbons (Table 4), it is to be noted that the commercial carbons were specified for use in water purification and not for decolorization.

The types of commercial markets suggested by the Wichita State University report (37) were decolorizers and water purification, both municipal and industrial. Currently, carbons produced by the methods tested could not compete commercially in any of these areas. It is

doubtful that a commercially competitive decolorizing carbon can be produced from the coke tested. It seems possible, however, that further modifications of the phosphoric acid-steam activation procedure could produce a low quality commercial grade carbon for use in water and/or gas purification.

6.2 Recommendations

If it is decided to continue the study, the following recommendations are offered:

Phosphoric Acid-Steam Activation:

Two modifications of the phosphoric acid-steam process are proposed:

1. Replace the steel reaction tube with a ceramic tube or a ceramic lined steel tube. During heating of the phosphoric acid treated samples, some phosphoric acid reacted with the steel reactor tube forming iron phosphate. Therefore, it is unknown just how much phosphoric acid was available for oxidation of the coke sample.

2. Attempt activation by starting with the liquid feed to the Skelly Oil Company coking unit, carbonizing the liquid in the presence of phosphoric acid and then steam activating the prepared coke. This is suggested because most chemical treatments are applied to the source material prior to carbonization. Also, the phosphoric acid could develop a

more porous coke which would permit better steam penetration
during final activation and thus possibly produce a better
quality activated carbon.

Chemical Treatments

The addition of metallic chlorides could improve adsorptive proper-
ties of the carbon. The use of calcium, magnesium, and zinc chlorides have
been effective in producing activated carbons from wood sawdust and peat.
The metallic chlorides should be added to the petroleum liquid mixture and
then carbonized. Phosphoric acid and/or sulphuric acid could also be added.
After carbonization, steam activation could then be employed.

Control Testing - Phenol Test

If further activation attempts prove successful, it is recommended
that the phenol adsorption test be included. The phenol test is a recog-
nized test used by the activated carbon industry. It evaluates carbons
for possible use in water purification. A description of the test may be
found in books by Hassler (10) and Mantell (18).

Final Observations

It is believed that an activated carbon of adequate quality can be
produced at least on a laboratory scale. Whether it is technically and
economically feasible to produce the carbon commercially will depend upon
the activation procedure finally adopted. It is believed that results
obtained to this date, indicate that the study be continued at least until
the proposed activation modifications have been attempted in the
laboratory.

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BIBLIOGRAPHY

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APPENDIX I

FIGURES, TABLES AND EXHIBITS

* Nitrogen   Water

Cylinder   Surge Tank

Boiler

I
Condenser

J
Condensate
Accumulator

K
Wet Test Meter

E

Furnace

T.R.C.

L

Reactor   Superheater

T.R.

G

H

*See Table 1 for Description and specification of Equipment.
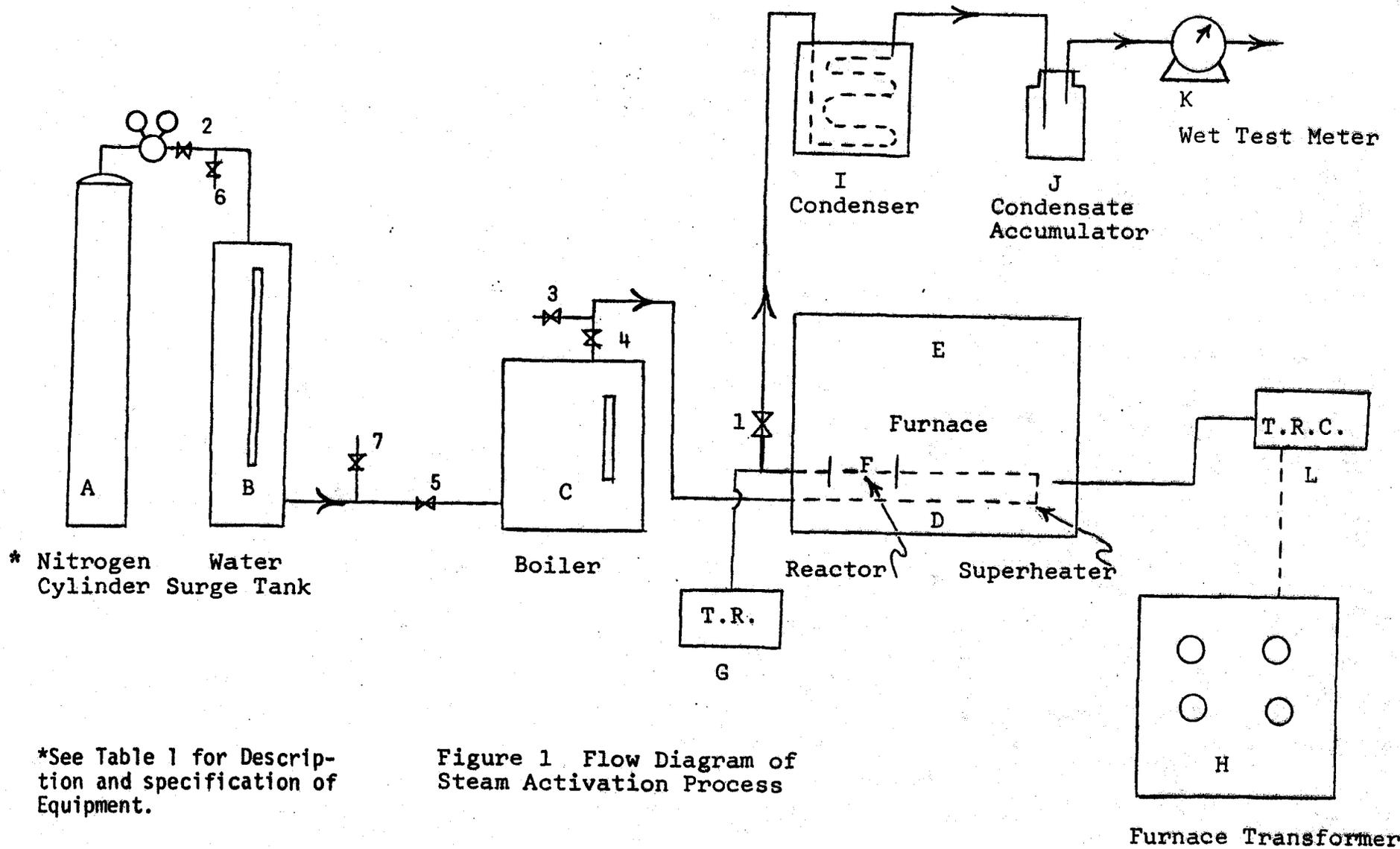
Figure 1   Flow Diagram of Steam Activation Process

Furnace Transformer

38
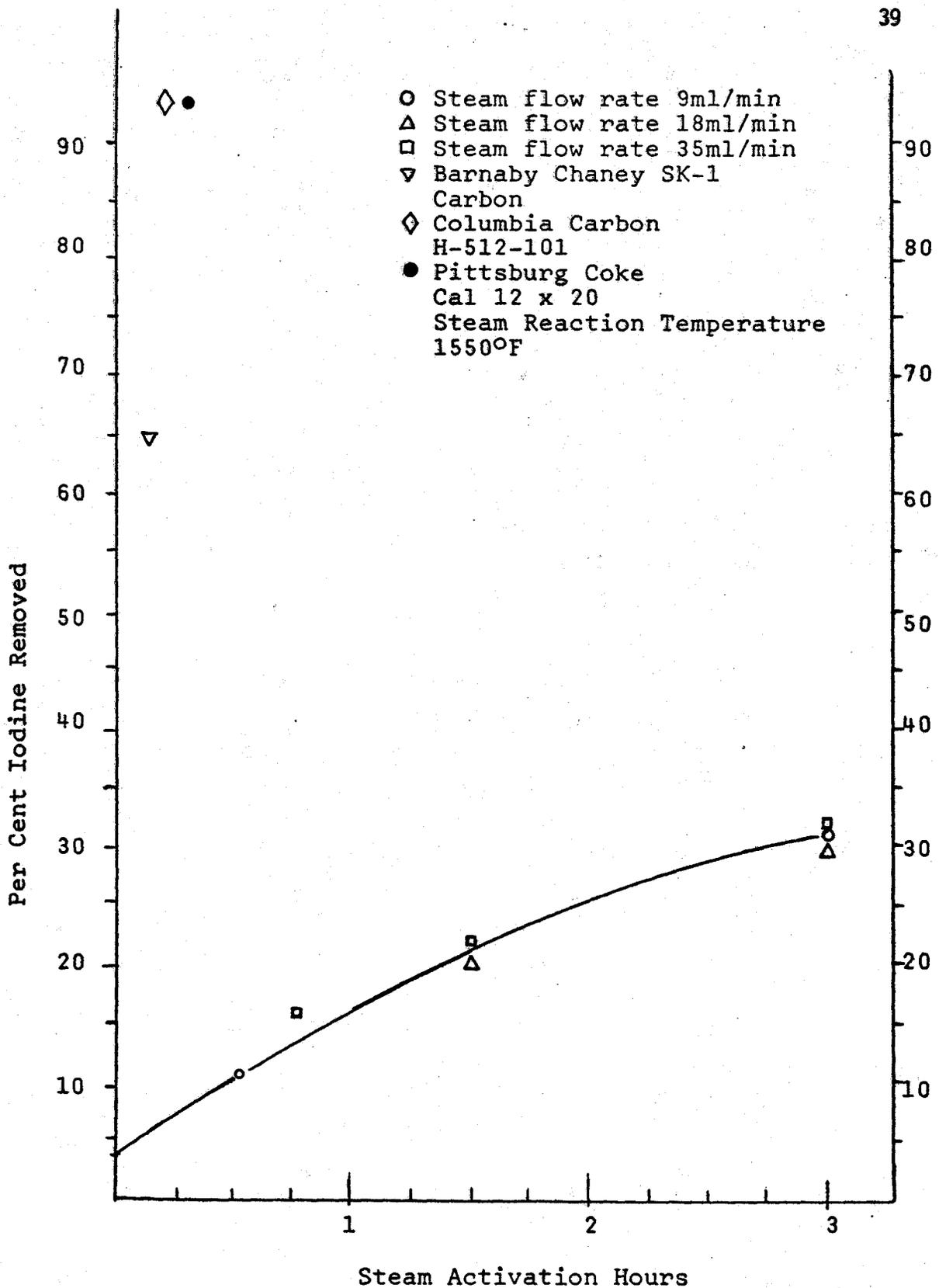
Figure 2   Effect of the Steam Flow Rate on Degree
of Carbon Activation as Indicated by Per
Cent Iodine Removed. (Data listed in
Table 2)

O Steam flow rate 9ml/min
△ Steam flow rate 18ml/min
□ Steam flow rate 35ml/min
▽ Barnaby Chaney SK-1

Per Cent Iodine Removed

1550°F

1650°F

1450°F

Steam Activation Hours
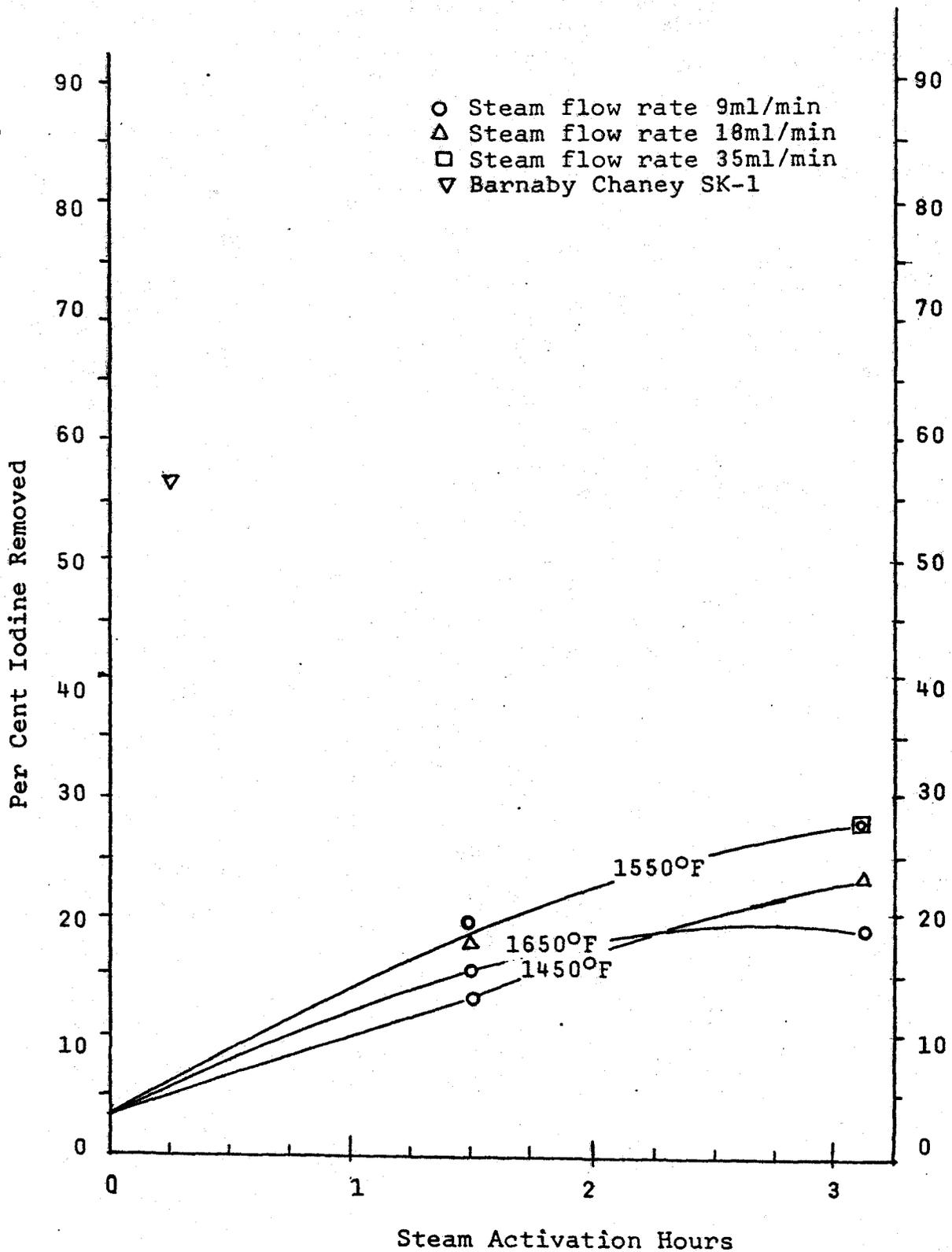
Figure 3   Reaction Temperature Effect on Degree of
            Carbon Activation as Indicated by Per
            Cent Effect Iodine Removed. (Data listed
            in Table 3)
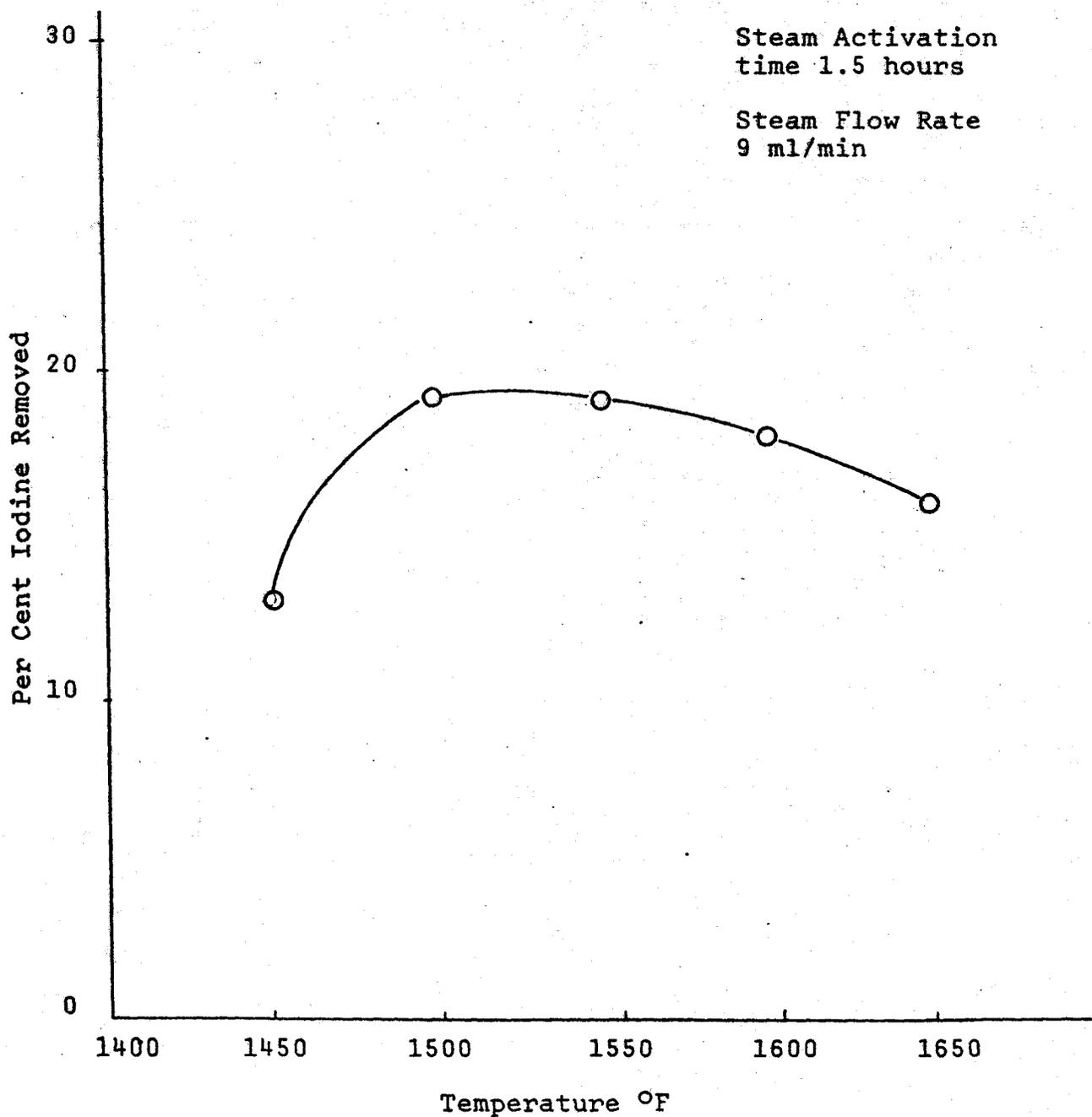
Figure 4 · Temperature vs. Per Cent Iodine Removal at
1.5 Hours Steam Activation and Constant Flow
Rate of 9ml/min (Date listed on Table 3)
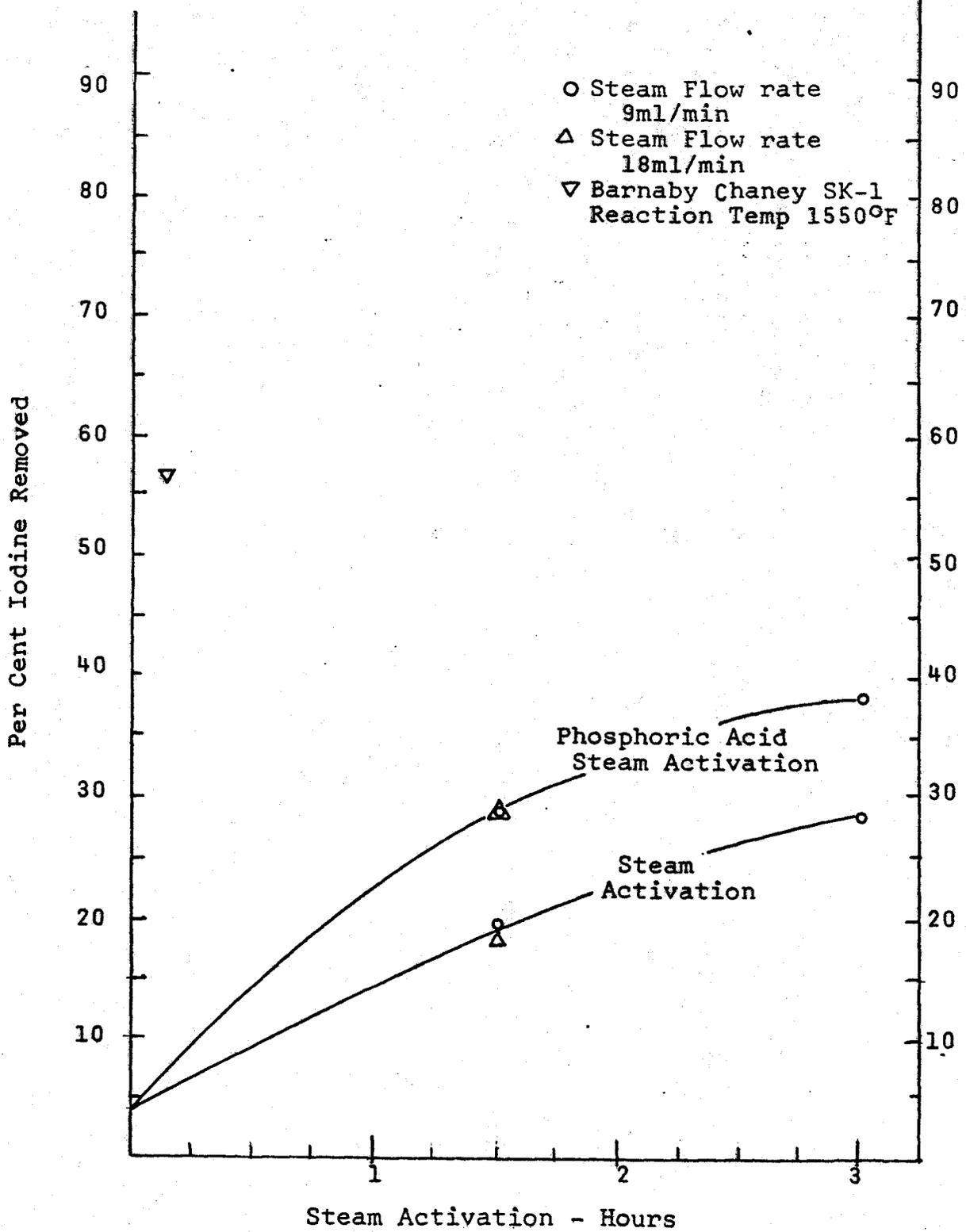
Figure 5   Comparison of Degree of Carbon Activation
for Steam vs. Phosphoric Acid-Steam
Treatments (Data Listed in Table 3)
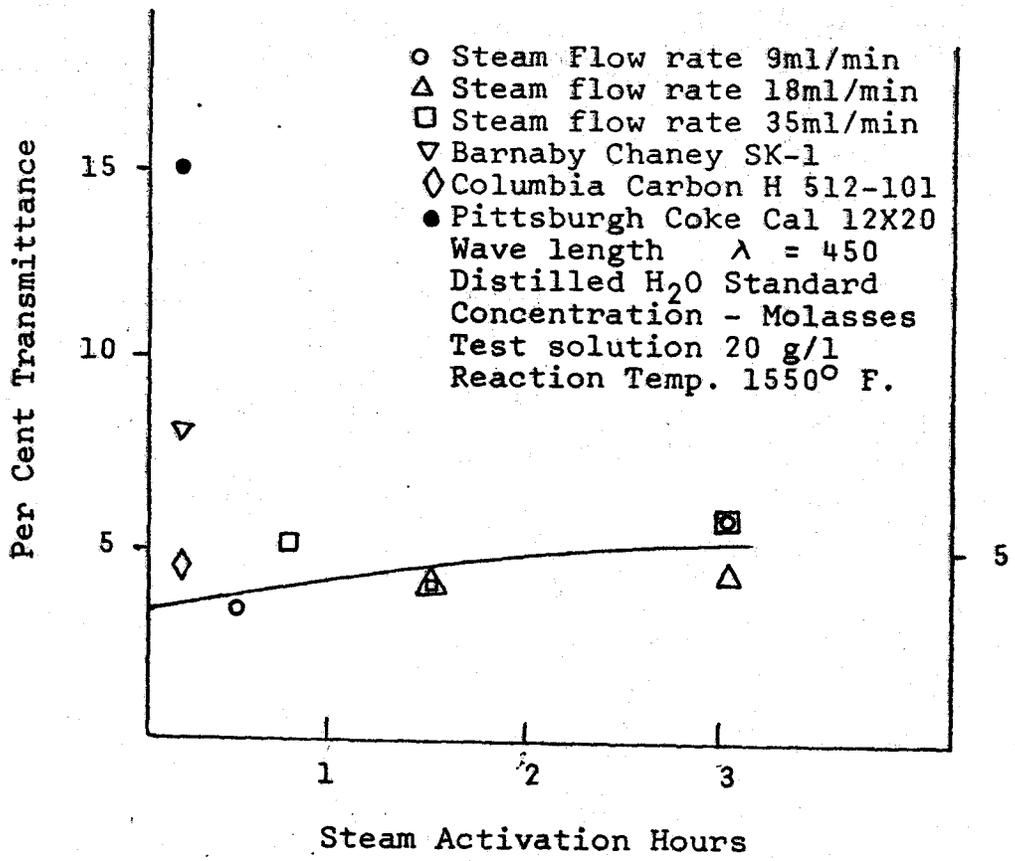
Figure 6   Percent Light Transmittance
            Vs. Hours Activation @ 1550°F
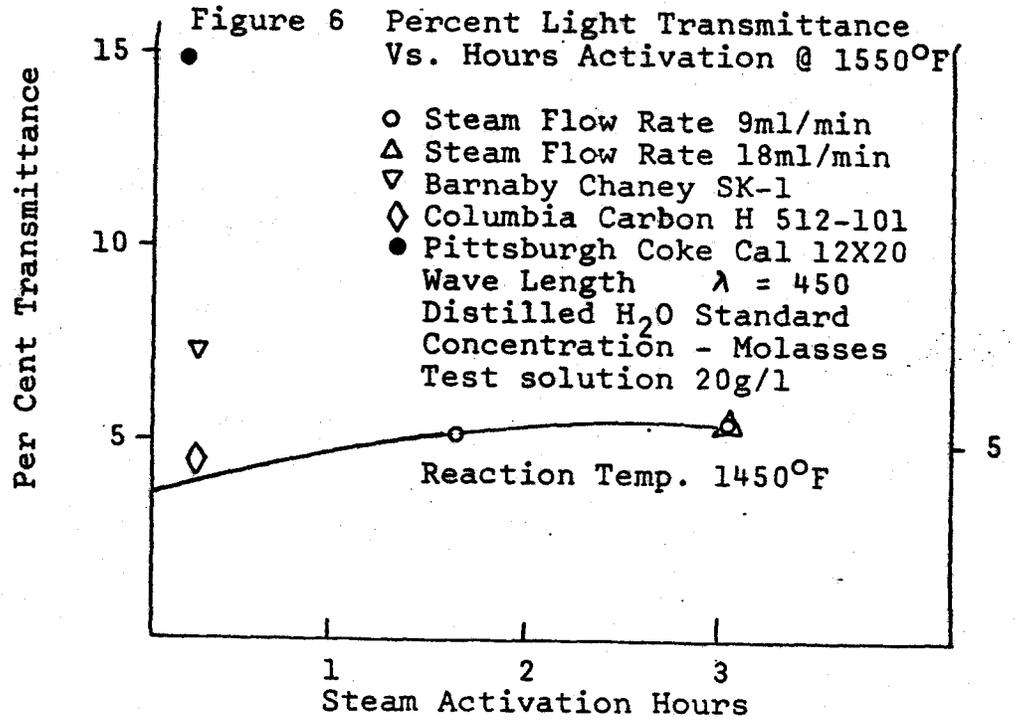
Figure 7   Per Cent Light Transmittance
           Vs. Hours Activation @ 1450°F
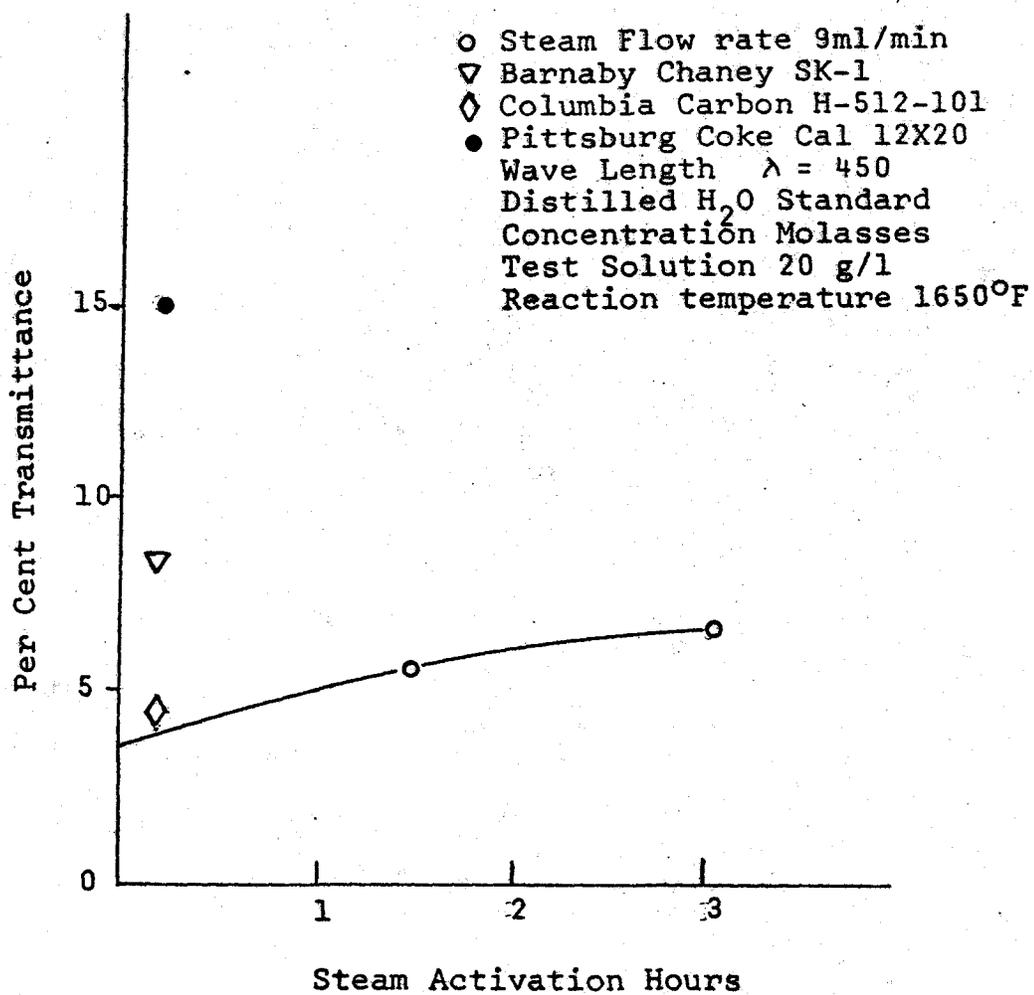
Figure 8   Per Cent Light Transmittance
Vs. Hours Activation @ 1650°F

Exhibit 1 Exit Steam Thermocouple Probe

Exhibit 2 Thermocouple-Steam Flow Rate Control Assembly

Exhibit 3   Reaction Tube
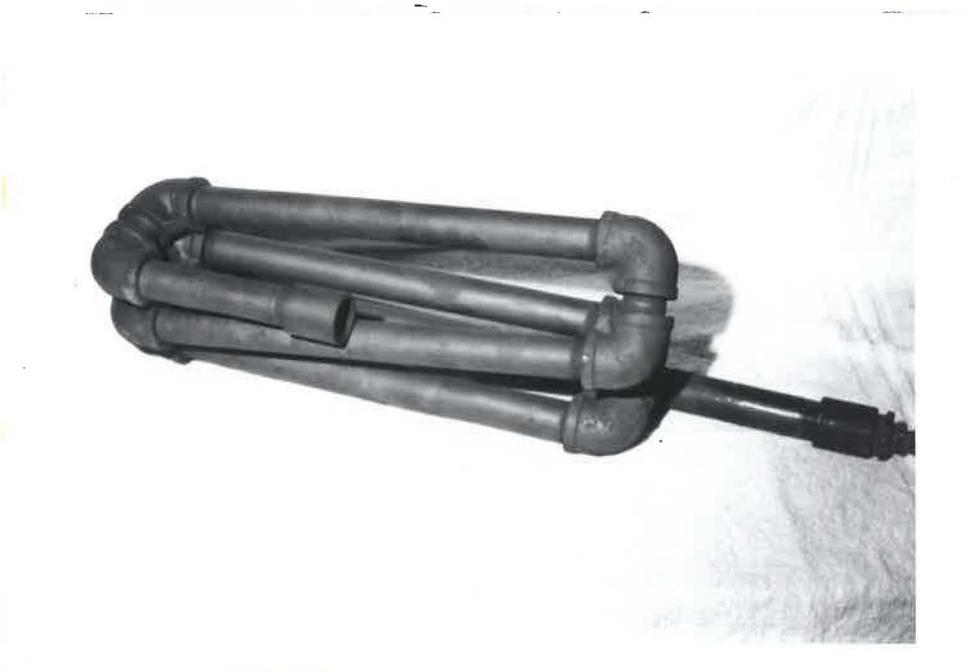
Exhibit 4   Super Heater Section
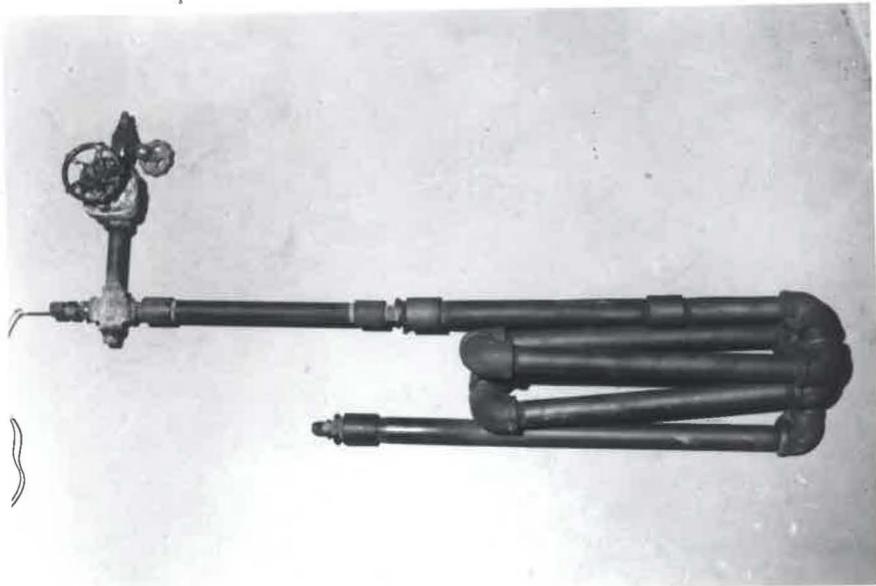
Exhibit 5   Superheater, Reactor, and Thermocouple
Steam Flow Rate Control Equipment – Assembled
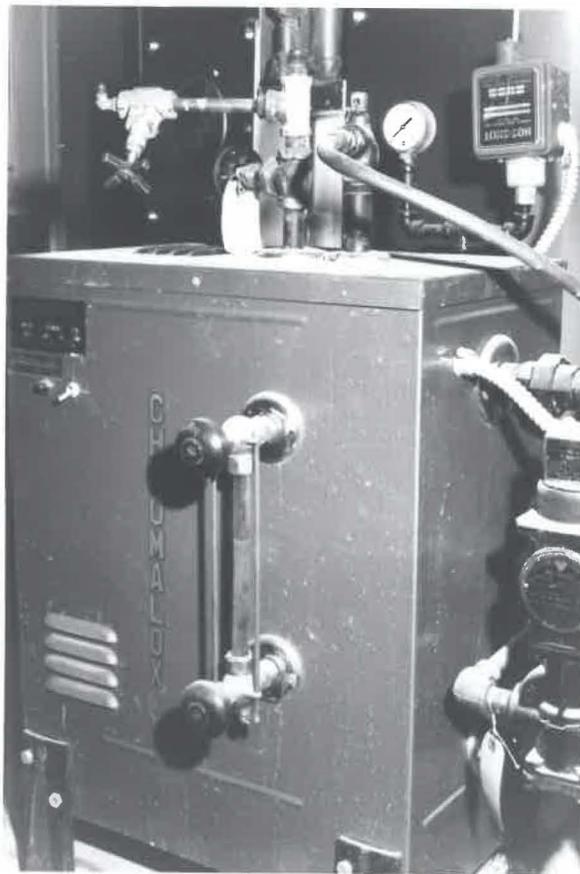
Exhibit 6 – Boiler

Exhibit 7   Nitrogen Cylinder and
Water Surge Tank

Exhibit 8   Front View Harper Electric
Furnace

Exhibit 9 Assembled Process Equipment
Showing Boiler Furnace, Steam
Condenser, Condensate Accumulator,
and Wet Text Meter

Exhibit 10 Harper Electric Furnace,
Transformer and Temperature
Recorder Controller

Exhibit 11 Gas Analysis

SKELLY OIL COMPANY

El Dorado, Kansas 67042

January 20, 1967

Mr. Don Green, Associate Professor
Department of Chemical Engineering
University of Kansas
Lawrence, Kansas

Dear Mr. Green:

Analyses of two samples of our refinery coke gave the following carbon, hydrogen results:

	Sample Date	% C	% H
Sample No. 1	10-17-66	90.96	3.76
		91.19	3.60
Sample No. 2	1- 5-67	91.94	4.30
		91.68	4.13

Sample No. 2, as shipped to analytical laboratory, also gave the following additional analyses:

Volatile Materials - 9.6%
Sulphur   - 1.65%
Ash   - 0.182%

The samples were ground and dried one hour in the oven at 100°C. but the analyses indicate that there may still be moisture present. Water is used to remove coke in the manufacturing process.

We hope this meets with your approval, and wish you every success in your program to activate samples of our refinery coke.

Yours very truly,

E. D. Flickinger

EDF:al

cc: W. H. Baker
     R. V. Struebing

Exhibit 12

Vickburg

SKELLY OIL COMPANY

El Dorado, Kansas 67042

September 22, 1967

Dr. D. Green
Chemical Engineering Department
University of Kansas
Lawrence, Kansas

Dear Dr. Green:

During the September meeting of the El Dorado Micro Planning
Industrial Development Group, Mr. Karl Vickburg asked if we
would analyze two samples of activated carbon which he had
prepared. We were happy to do so, and the results are as
follows:

Sample Number	% Carbon	% Hydrogen
7	93.91	0.95
	94.08	0.96
21	92.75	0.87
	92.66	0.90

Hoping for the continued success of the activated carbon project,
we remain,

Very truly yours,

E. D. Flickinger

EDF:al
cc: R. V. Struebing
     W. H. Baker

Exhibit 13

KANSAS GEOLOGICAL SURVEY
QUALITATIVE SPECTROGRAPHIC ANALYSIS

Qual Anal on Coke from Skelly
Oct. 24, 1966

Submitted by _Wayne_
Sample of _Pet. Mining Coke_

SAMP. NO. __66 507__   FILM # __6110-241__

Wave L.	Pres	Ck. Wave L.	Pres	Rel	El	Wave L.	Pres	Wave L.	Pres
2349.8		2780.2			Rh	3323		3397	
2478		------			Ti	3341		3349	
2497		2498			Sc	3353		3912	
2516		2882			Zr	3391		3438	
2534		2535			Pd	3405R		3421R	
2576		4030 r			Co	3405 R		3453R	
2598.3		2528.5			Ni	3415 R		3493 R	
2659		3064 R			K	3446		3447	
2427 R		2676 R			Re	3460W		------	
2678		3436 R			Tm	3462		3761	
2741		3232 R			Sr	3465		4077	
2768		3519 R			Er	3692		3906	
2795		2852 R			Tb	3561		3874	
2919		3072			Gd	3646w		4251	
2833 R		3683			Hg	2536 R		4358 w	
2840 R		3175 h			U	4241		3672	
2898 WR		3068.hR			Ca	3933 R		3968 R	
2900 R		3058 R			Al	3944		3961	
2911		3472			La	3949		3988	
3220		3513			Nd	3952		4174	
3891		3748			Dy	4000		4211	
2943		4032 R			Ce	4186		4222	
2947		4008			Th	4019		3601	
3020 R		3581 R			Pr	4179		4223	
3039		3269			Ev	3907 W		4205 R	
3071 R		4130			Rb	4201 R		4215 R	
3094		4058			Cr	4254 R		4274 R	
2348 R		3321 r			Te	2383		2385	
3132		3170 R			Sm				
3185		3183							
3242		3710							
3247 R		3274 R							
3256 R		4102 R							
2288 R		3466							
3281 R		3383 R							
3282		3345							
3290		3694 R							
3302 R		3303 R							
3311 w		2714							

REMARKS

Have Karm wet ash 50ml 10 g

$\mathcal{L} = < 0.1 \%$
$T = 0.1 - 1\%$
$m = 1 - 10\%$

Analyzed by: _W E K__

Exhibit 14

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Table 1

Steam Activation Process
Major Equipment Test

Item	Equipment	Purpose	Description
A	Commercial nitrogen gas cylinder	Force water to boiler; purge coke samples of volatiles during heating of furnace	Standard 220 ft^3 nitrogen cylinder
B	Distilled water surge tank	Water supply to boiler	Galvanized iron; Capacity 18 gal; 1 ft. X 3 ft. cylinder, elliptical heads; 2 ft. sight glass
C	Chromalox boiler	Supply Steam for Activation Process	Model C.E.S. -6, Serial No. K-1040, Power Source electric, 240 volt, 3 phase 60 cycle, 15 amp, Working Pressure 0-20 psig
D	Steam superheater	Super heat steam from boiler exit temperature to desired reaction temperature	1 in. O.D. pipe; schedule 40; Stainless steel 304, total length 10 ft., filled with alumina cylinders ½ in X 3/8 in. Threaded connections
E	Harper Electric Furnace	Heat source for superheating steam; maintain desired temperature in the reactor	Furnace Model H-S 4.5912 -LT, Temperature Range 0-2900°F, Power Service 230 volt, 60 cycle, 3 phase

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Item	Equipment	Purpose	Description
F	Reactor	Hold coke test sample; reaction zone	1 in. O.D. pipe; schedule 40; stainless steel 304; threaded connections
G	Exit Steam temperature Probe and recorder	Record temperature of exit steam from reactor	Honeywell-Brown Electronic recorder, Model 153 X 17 P X-30, Serial No. 552-N, Range 0 - 2000°F, Thermocouple Probe Alumel, Chromel thermocouple wire 20 gauge; length 21 in.; wires protected with ceramic insulators; junction covered with saureisen cement
H	Harper Electric Furnace Transformer	Power source for electric furnace	Capacity 30 KVA, Input 230 volt, 60 cycle, 3 phase
I	Steam Condenser	Condense exhaust steam from steam condenser	$\frac{1}{4}$ in. diameter copper tubing; length 12 ft.; placed in water filled tank.
J	Condensate Accumulator	Collect condensed steam from steam condensor	5 gal. glass jar, narrow necked.
K	Precision wet test meter	Measure gas flow from the reactor	Model 11 - T - 4
L	Bristol Temperature Recorder controller	Control furnace temperature	Model M-1 PG 565 FBT - 100 Serial Number 544251, Range 0 - 3000°F, thermocouple probe-platinum-rhodium 10%

Item	Equipment	Purpose	Description
1	Needle valve	Control steam flow rate to the reactor	¼ in. stainless steel needle vavle; threaded connections
2	Needle valve	Valve for connection of copper tubing to water surge tank	¼ in. brass needle valve; threaded connection
3	Needle valve	Boiler steam vent and nitrogen purge connection	¼ in. stainless steel needle valve; threaded connections
4	Gate valve	Boiler exit steam control valve	½ in. brass gate valve; threaded connection
5	Gate valve	Boiler water supply control valve	½ in. brass gate valve; threaded connection
6	Needle valve	Nitrogen vent	½ in. brass gate valve; threaded connection
7	Gate valve	Water surge tank drain control valve	½ in. brass gate valve; threaded connection

Table 2
Steam Activation
Iodine Test Results

Sample	Activation Temp °F	Steam Flow Rate cc/min	Activation Time-hrs.	Iodine Removed g/l	% Iodine Removed	% Carbon Recovery	Comments
Iodine Stock Solution				21.02*			* Iodine g/l = 2.102 stock soluti‹
Columbia Carbon H-512-101	–	–	–	19.69	94	–	
Barnaby & Chaney SK-1	–	–	–	13.79	66	–	
Pitt Coke Cal 12X20	–	–	–	19.50	93	–	
El Dorado Pet. Coke Untreated	–	–	–	0.9	4	–	
2	1650	35	0.5*	3.80	18	48.5	*Steam turned c prior to reaching 1650°F actual length of time of steam activation unknown
3	1650	45.9	1.5	2.73	13	29.6	
4	1550	35	1.5	4.64 4.59	22 22	55.5	
5	1550	18	3	6.29	30	50.9	
6	1550	8	0.5	2.31	11	78.3	
7	1550	18	1.5	4.32 4.20	20 20	60.9	
8	1550	9	3	6.60	31	41.7	

Sample	Activation Temp °F	Steam Flow Rate cc/min	Activation Time-hrs.	Iodine Removed g/l	%Iodine Removed	%Carbon Recovery	Comments
9	1550	35	0.75	3.40	16	74.7	
10	1550	35	3	6.82	32	17.9	
11	1450	9	3	4.91	23	66.8	
12	1450	9	1.5	3.19	15	78.3	

Table 3

Steam Activation and Steam-Phosphoric Acid Activation
Iodine Test Results

Sample	Activation Temp °F	Steam Flow Rate ml/min	Activation Time hrs.	Iodine Removed g/l	% Iodine Removed	%Carbon Recovery	Comments
Iodine Stock Solution				24.46*			* Concentration of iodine stock solution was 24.46 g/l
El Dorado Pet Coke Untreated				1.0	4		
7	1550	18	1.5	4.36	18	60.9	
8	1550	9	3	6.86	28	41.7	
10	1550	35	3	6.96	28	17.9	
12	1450	9	1.5	3.28	13	78.3	
13	1450	18	3	5.67	23	56.3	
14	1650	9	3	4.56	19	12.6	
15	1650	9	1.5	3.80	16	43.3	
16	1600	9	1.5	4.46	18	52.3	
17	1500	9	1.5	4.76	19	65.7	
18	1550	18	1.5	7.04	29	44.3	Phosphoric Acid-Steam Activation (H_3PO_4 conc. 85% by wt.)
19	1550	9	3	9.41 9.25	38 38	25.4	Phosphoric Acid-Steam Activation (H_3PO_4 conc. 85% by wt.)

Sample	Activation Temp °F	Steam Flow Rate ml/min	Activation Time hrs.	Iodine Removed g/l	%Iodine Removed	% Carbon Recovery	Comments
20	1550	18	1.5	6.28	25	42.3	Phosphoric Acid-Steam Activation (H_3PO_4 conc. 55% by wt.)
21	1550	18	1.5	5.76	23	41.7	Carbon boiled in concentrated phosphoric Acid (H_3PO_4 conc. 85% by wt.) for 3 hrs. then steam treated.
22	1550	9	1.5	4.73	19	59.4	
A				1.42	6		Carbon boiled in concentrated phosphoric acid (H_3PO_4 conc. 85% by wt.) no steam treatment.
Barnaby & Chaney SK-1	-	-	-	13.98	57		

Table 4

Steam Activation and Phosphoric Acid-Steam Activation
Molasses Test Results

Sample	Activation Temperature $^{\circ}$F	Steam Flow Rate ml/min	Activation Time-Hrs.	% Transmittance[1]	% Transmittance [2]
Columbia Carbon H-512-101	-	-	-	4.5	-
Barnaby Chaney SK-1	-	-	-	8	16.9
Pittsburg Coke Cal 12 x 20	-	-	-	15	28.5
El Dorado Pet. Coke Untreated	-	-	-	3.5	12
2	1650	35	-	4	-
3	1650	45.9	1.5	4	-
4	1550	35	1.5	4	-
5	1550	18	3	4	-
6	1550	8	0.5	3.5	-
7	1550	18	1.5	4	-
8	1550	9	3	5.5	13
9	1550	35	0.75	5.0	-
10	1550	35	3	5.5	-
11	1450	9	3	5.2	-

Sample	Activation Temperature °F	Steam Flow Rate ml/min	Activation Time-Hrs.	% Transmittance [1]	% Transmittance [2]
12	1450	9	1.5	5.3	-
13	1450	18	3	5.5	-
14	1650	9	3	5.9	-
15	1650	9	1.5	5.3	-
16	1600	9	1.5	5.9	-
17	1500	9	1.5	4.9	-
18 [3]	1550	18	1.5	-	13
19 [3]	1550	9	3	-	14
20 [4]	1550	18	1.5	-	13.8
21 [5]	1550	18	1.5	-	13.1
22	1550	9	1.5	-	-
A [6]	-	-	-	-	18
B [7]	-	-	-	-	16

(1) Molasses test solution concentration 20 g/l; λ = 450; Transmittance standard distilled water.
(2) Molasses test solution concentration 15 g/l; λ = 450; Transmittance standard distilled water.
(3) Phosphoric Acid-steam activation (H_3PO_4 conc. 85% by weight).
(4) Phosphoric Acid-steam activation (H_3PO_4 conc. 55% by weight).
(5) Carbon boiled in concentrated H_3PO_4 (85% by weight) for 3 hours then steam heated.
(6) Coke sample boiled in concentrated phosphoric acid (85% by weight) for 3 hrs. no steam activation.
(7) Coke sample boiled in phosphoric acid (conc. 55% by weight) for 3 hrs. no steam activation.

Table 5

Steam Activation and Steam-Phosphoric Acid Activation Process Data

Sample	Activation Temp. $^\circ$F	Steam Flow Rate ml/min	Activation Time Hrs.	Weight of Carbon Sample grams	Weight of Treated Carbon grams	Reactor Exit Gas Accumulation Ft^3	Reactor Exit Gas Temp. $^\circ$
2	1650	35	unknown	72.9	35.3	-	-
3	1650	45.9	1.5	63.4	18.8	-	-
4	1550	35	1.5	69.9	38.8	4.5*	82
5	1550	18	3	67.2	34.2	3.1*	80
6	1550	8	0.5	64.0	50.2	1.1*	83
7	1550	18	1.5	64.5	39.3	3.9*	86
8	1550	9	3	64.1	26.7	5.0*	83
9	1550	35	0.75	64.1	47.9	2.3*	87
10	1550	35	3	64.1	11.5	8.9*	85
11	1450	9	3	64.1	42.8	2.6	87
12	1450	9	1.5	64.1	50.3	1.6	85
13	1450	18	3	64.1	36.0	-	-
14	1650	9	3	64.1	8.1	8.0	83
15	1650	9	1.5	64.1	27.7	4.2	86
16	1600	9	1.5	64.1	33.6	5.2	83

Sample	Activation Temp. °F	Steam Flow Rate ml/min	Activation Time Hrs.	Weight of carbon sample grams	Weight of Treated Carbon Grams	Reactor Exit Gas Accumulation Ft.	Reactor Exit Gas Temp. °F
17	1500	9	1.5	64.1	42.1	3.1	85
18[1]	1550	18	1.5	64.1	28.4	5.6	87
19[1]	1550	9	3	64.1	16.2	7.6	80
20[2]	1550	18	1.5	64.1	27.0	5.9	80
21[3]	1550	18	1.5	64.1	26.7	5.8	80
22[4]	1550	9	1.5	64.1	38.1	4.05	80

* Based on average gas flow rate (Ft^3/ hour) for the activation period.

(1) Phosphoric Acid-Steam Activation (H_3PO_4 - concentration - 85% by weight. 10 grams mixed with test sample).

(2) Phosphoric Acid-Steam activation (H_3PO_4 - concentration - 55% by weight 10 grams mixed with test sample).

(3) Carbon boiled in concentration phosphoric acid (85% by weight) for 3 hrs. then steam treated.

(4) Barometric Pressure 745.2 mm Hg.

Table 6

Data

Solium Thiosulfate Solution Standardization

Sample	Normality Potassium Dichromate	ml Potassium Dichromate	ml Sodium Thiosulfate	Comments
A	0.1000	20	20.1	Sodium thiosulfate
	0.1000	20	19.60	solution used for
	0.1000	20	19.68	test samples listed in Table 2.
B	0.1000	20	20.05	Sodium thiosulfate
	0.1000	20	20.07	solution used for carbon test samples listed in Table 3.

Table 7

Data

Iodine Solution Standardization

Sample	ml Iodine	Normality Sodium Thiosulfate	ml Sodium Thiosulfate	Comments
A	25	0.1018	40.68	Iodine solution
	25	0.1018	40.65	used for carbon
	25	0.1018	40.70	test samples listed in Table 2.
B	25	0.09975	48.32	Iodine solution
	25	0.09975	48.30	used for carbon
	25	0.09975	48.26	test samples listed in Table 3.

Table 8

Data

Iodine Test (For Samples Listed in Table 2)

Sample	ml Iodine*	ml Sodium Thiosulfate **
Columbia Carbon H-512-101	25	2.58
Barnaby Chaney Sk-1	25	14.00
Pittsburg Coke Cal 12 x 20	25	2.90
El Dorado Petroleum Coke Untreated	25	38.97
2	25	33.32
3	25	35.40
4	25	31.70
5	25	31.80 28.50
6	25	36.20
7	25	32.40
8	25	32.70 27.90
9	25	34.10
10	25	27.50
11	25	31.18
12	25	34.50

* Iodine concentration 21.02 g/1 - Standardization data shown in Table 7, Sample A.

** Sodium Thiosulfate normality 0.1018 - Standardization data shown in Table 6, Sample A.

Table 9

Data

Iodine Test (For Samples Listed In Table 3)

Sample	ml Iodine*	ml Sodium Thiosulfate**
El Dorado Petroleum Coke Untreated	25	46.40
Barnaby Chaney SK-1	25	20.7
7	25	39.70
8	25	34.75
10	25	34.50
12	25	41.60
13	25	37.10
14	25	39.30
15	25	40.80
16	25	39.50
17	25	38.90
18	25	39.70
19	25	29.71 30.04
20	25	35.90
21	25	36.90
22	25	39.00
A	25	45.50

* Iodine concentration 24.46 g/l - Standardization data shown in Table 7, Sample B.

** Sodium Thiosulfate Normality 0.09975 - Standardization data shown in Table 6, Sample B.

Table 10

Data
Molasses Test

Sample	Percent Transmittance[1]	Percent Transmittance[2]
Columbia Carbon H-512-101	4.5	---
Barnaby Chaney SK-1	8	16.9
Pittsburg Coke Cal 12x20, El Dorado	15.	28.5
Petroleum Coke un-treated	3.5	12.
2	4	---
3	4	---
4	4	---
5	4	---
6	3.5	---
7	4	---
8	5.5	13.
9	5.0	---
10	5.5	---
11	5.2	---
12	5.3	---
13	5.5	---
14	5.9	---
15	5.3	---
16	5.9	---
17	4.9	---
18[3]	---	13
19[3]	---	14
20[4]	---	13.8
21[5]	---	13.1
22	---	---
A[6]	---	18
B[7]	---	16

1. Molasses test solution concentration 20 g/l; $\lambda = 450$; Transmittance standard distilled water.
2. Molasses test solution concentration 15 g/l; $\lambda = 450$; Transmittance standard distilled water.
3. Phosphoric acid-steam activation (H_3PO_4 conc. 85% by wt.)
4. Phosphoric acid-steam activation (H_3PO_4 conc. 55% by wt.)
5. Carbon boiled in conc. H_3PO_4 (85% by wt.) for 3 hours, then steam heated.
6. Coke sample boiled in conc. phosphoric acid (85% by wt.) for 3 hrs., no steam activation.
7. Coke sample boiled in phosphoric acid (conc. 55% by wt.) for 3 hours, no steam activation.

APPENDIX   II

LABORATORY TEST PROCEDURES AND CALCULATIONS

A. IODINE ADSORPTION TEST

The iodine test procedure adopted was obtained from the West Virginia Pulp and Paper, Chemical Division (13). The calculational procedure was obtained from Mantell (18).

1. Reagents

   "Iodine solution = $\pm$ 0.1 grams Iodine (I_2) per liter, dissolved with 38 grams potassium iodide (KI) per liter in tap water. Sodium Thiosulfate Solution N/10 - 25 grams $Na_2S_2O_3 \cdot 5H_2O$ per liter distilled water. (Standardized.)"

2. Procedure

   a. "Weigh 1.00 grams of dry carbon and place in a 250 ml. Erlenmeyer Flask (open mouth).

   b. Add 50 ml. iodine solution.

   c. Swirl to wet carbon and swirl for one additional minute.

   d. Filter immediately and completely by gravity through a No. 2V fluted Whatman 18.5 cm. filter paper.

   e. Pipette 25 ml. of filtrate into a 150 ml. beaker, titrate with N/10 Sodium Thiosulfate (no starch necessary)."

3. Evaluation

$$\frac{(g.iodine/l. \ in \ stock \ sol.)-(g.iodine/l. \ in \ carbon\text{-}treated \ sample)}{g.iodine/l. \ in \ stock \ solution}$$

   X 100 = % iodine removed.

4. Standardizations and Calculations - Iodine Test

   a. Standardization of Sodium Thiosulfate.

   Normality of Sodium Thiosulfate - Standardized against

71

0.1 N Potassium dichromate.

ml X normality = ml X normality (Data Table 6-A)

$19.60 \times N_{Na_2S_2O_3 \cdot 5H_2O} = 20 \times 0.1 \, N_{K_2Cr_2O_7}$

$N_{Na_2S_2O_3 \cdot 5H_2O} = 0.1020$ equivalents/liter

$19.68 \times N_{Na_2S_2O_3 \cdot 5H_2O} = 20 \times .1$

$N = 0.1016$ equivalents/liter

Avg $N_{Na_2S_2O_3 \cdot 5H_2O} = 0.1018$ equivalent/liter

b. Standardization of Iodine stock solution (concentration g/l).

Normality iodine solution (Data Table 7-A)
ml X normality = ml X normality
$25 \times N_{Iodine} = (40.68)(0.1018)$

$N_{Iodine} = 0.1656$ equivalents/liter

Iodine concentration g/l

$$0.1656 \, \frac{eq.iodine}{liter} \times \frac{mole \ iodine}{eq.iodine} \times \frac{126.92 \ g.iodine}{mole \ iodine}$$

$$= \frac{21.02 \ g.iodine}{liter}$$

c. Per Cent Iodine Removed (Table 8, sample 8)

Normality of carbon treated iodine solution

$$N = \frac{27.90 \ (0.1018)}{25}$$

$N = 0.1136$ equivalents/liter

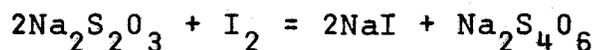Concentration of iodine solution

$0.1136 \times 126.92 = 14.42$ g/l

Per Cent Iodine removed

$$= \frac{g/l \ iodine \ stock \ sol. - g/l \ iodine \ treated \ sol. \times 100}{g/l \ iodine \ stock \ solution}$$

$$\frac{21.02 - 14.42}{21.02} = 31\% \text{ iodine removal.}$$

5. <u>Iodimetry</u> (35)

"The fundamental reaction of iodimetry is the following:

$$2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6$$

or

$$2S_2O_3^{--} + I_2 \quad 2I^- + S_4O_6^{--}$$

If to a solution containing a little iodine some starch solution is added, and sodium thiosulfate solution is run in from a buret, the blue color of the iodo-starch will disappear from the solution as soon as all the iodine has been reduced to iodide in accordance with the above equation. This is one of the most sensitive reactions used in analytical chemistry. If, therefore, a sodium thiosulfate solution of known strength is at hand, we have a means of determining not only iodine itself, but all those substances (oxidizing agents) which when treated with potassium iodide set iodine free, or when acted upon by hydrochloric acid evolve chlorine. Consequently, iodimetric processes are not only accurate, but also capable of most general application."

6. <u>Standardization of Sodium Thiosulfate Solution (35)</u>.
With Potassium Dichromate:

"The reaction between potassium dichromate and potassium iodide can also be used for the standardization of sodium thiosulfate solutions; the dichromate is reduced to green chromic salt and an equivalent weight of iodine being set free

provided that the solution is 0.2-0.4 N in acid.

$$Cr_2O_7^{--} + 6I^- + 14H^+ \quad 2Cr^{++} + 3I_2 + 7H_2O$$
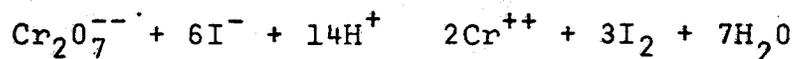
Prepare tenth-normal potassium dichromate solution by dissolving 4.903 g. of pure dry salt in water and diluting to 1 liter at 20° C in a measuring flask. Mix well by pouring back and forth from the flask to a beaker at least 4 times. Measure out 20-40 ml of the dichromate solution with a pipet or buret, into a 500-ml beaker containing 50 ml of water, 10 ml of concentrated hydrochloric acid, and 3 g. of potassium iodide. Allow the reaction to proceed in the dark for 5 minutes, then dilute to 400 ml and titrate with tenth-normal thiosulfate solution, adding starch toward the last."

7. <u>Preparation of Sodium Thiosulfate Solution (35).</u>

"From the equation on p. 583 it is evident that an equivalent weight of iodine, the atomic weight in grams, is equal to 1 mole of $Na_2S_2O_3$. Hence, exactly 0.1 mole of crystallized sodium thiosulfate ($Na_2S_2O_3 + 5H_2O$) is required to make 1 liter of tenth-normal solution."

"A solution of pure sodium thiosulfate in doubly distilled water will keep very well, but thiosulfate solutions usually deposit sulfur on standing, and the titer changes until the decomposition brought about by impurities is complete. The principal cause of the decomposition is bacterial action. Sterile solutions, free from carbon dioxide, keep indefinitely.

The addition of about 3.8 g. of borax per liter helps to keep the solution sterile, but the solution should stand a week or so before determining its exact concentration."

"The molecular weight of $Na_2S_2O_3 \cdot 5H_2O$ is 248.19. To prepare 1 liter of 0.1 N solution, 24.82 g. of the salt is necessary, or, in round numbers, 25 g."

8. Standardization of Iodine Solution (35)

"Take 25 ml of the well-mixed iodine solution in a 250-ml Erlenmeyer flask, dilute to 100 ml and introduce 0.1 N $Na_2S_2O_3$ solution until nearly all the iodine has reacted as shown by the color. Add 1 ml of starch paste and titrate slowly until colorless."

9. The Starch Solution (28)

"To 2.5 grams of arrowroot or potato starch add a few milliliters of cold water, and rub up to a paste. Add this, with stirring, to 1 liter of boiling water, so slowly that boiling never ceases. Boil for an additional minute or two, and allow to cool. Preserve by the addition of 1 ml of chloroform. Keep in a glass-stoppered bottle. Discard and make up a new solution when mould appears or if a good strong color is not given with very dilute iodine solution."

B. MOLASSES TEST

The procedure used for the molasses test was suggested by Mantell (18). "The pH of a water extract of the carbon tested has a marked effect on this test. To get true comparisons between carbons, they should be adjusted to the same pH."

1. Reagents

"The solution of blackstrap molasses must be freshly prepared each day and kept in a cool place. Depending on the depth of color in the blackstrap, 25 to 50 g. is dissolved in a liter of distilled water. This solution is then filtered through a 1/2-in. layer of filter aid placed on a filter cloth in a Buchner funnel."

"Place 50 ml. of molasses solution in a 150-ml. beaker, add 0.5 g. of the dry carbon being tested, and stir until wetted. Bring the mixture to a boil, and filter immediately through a No. 5 Whatman paper, or its equivalent, in a gravity funnel."

2. Evaluation

The evaluation procedure suggested by Mantell was use of Nessler tubes or a Kennicott-Campbell-Hurley colorimeter. The author could not reproduce molasses test results satisfactorily using Nessler tubes and a colorimeter was unavailable. It was decided to use a Beckman Model B Spectrophotometer for this evaluation. Distilled water was selected as the standard and a light wavelength of 450 angstroms was used. Molasses

tests on commercial carbons were run for comparison purposes.
The data have been tabulated as per cent light transmittance.

C. Gas Analysis

1. Procedure

Reactor exit gas from test run No. 22 was analyzed to
determine its content of carbon dioxide, carbon monoxide
and hydrogen by using the gas analysis equipment shown
in Exhibit 11. The initial volume of the test sample
was determined in the gas measuring burette. Carbon
dioxide content was determined by repeatedly bubbling
the test sample through the sodium hydroxide filled gas
pipette. The decrease in the volume of the sample repre-
sented carbon dioxide removed by the sodium hydroxide.
The carbon dioxide-free sample was then passed to the
copper oxide gas combustion pipette, heated to 325° C.
Hydrogen in the sample was converted to water and carbon
monoxide converted to carbon dioxide. The decrease in
volume was again noted in the gas measuring burette.
The volume change accounted for the hydrogen in the
sample. The sample was again passed through the sodium
hydroxide filled gas pipette. The volume change repre-
sented the volume of carbon monoxide in the sample.

2. Sample 22 Gas Analysis Calculations

    a. Analysis Wet Basis

        33.1 ml gas sample - wet basis

Caustic   33.1
                 28.2
                  4.9 cc CO_2

Copper Oxide   28.2
                  10.1
                  18.1 cc H_2

Caustic   10.1
                 4.4
                 5.7 cc CO

Remaining Gas   4.4 cc

b. Analysis Dry Basis
(Atmosphoric Pressure 745.2 mm Hg., Gas Temperature 80° F.,
Table 5.)

Water Vapor Correction

V.P. H_2O @ 80° F = 26.3 mm Hg.

Correction factor, $\dfrac{26.3}{745.2}$ = 0.0353

Sample Volume Corrections - Dry Basis

Gas Sample = 33.1 X (1.00 - 0.0353)
           = 33.1 X 0.9647
           = 31.9 cc

CO_2 = 4.9 X 0.9647
           4.7 cc

H_2 = 18.1 X 0.9647
           17.5 cc

CO   = 5.7 X 0.9647
         = 5.5 cc

Remaining
  Gas   = 4.4 X 0.9647
           4.2 cc

3. Sample 22 Material Balance Calculations

Wt. of coke sample 64.1 g. (Table 5)

% volatiles in sample 9.6% (Appendix I Exhibit 12)

Atmosphoric Pressure 745.2 mm Hg. (Table 5)

Gas Temperature 80° F (Table 5)

(Assume volatiles are lost while heating sample)

Wt. of coke sample less volatiles = 64.1 X (1 - .096)
= 58.0 g. coke

Coke remaining after steam treatment = 38.1 g. (Table 5)

Carbon loss 58.0 - 38.1 = 19.9 g. loss

$19.9 \text{ g.} \times \frac{lb}{454 \text{ g}} = 0.0439$ lbs. carbon loss

From gas analysis - Ratio of mols CO_2 and CO

4.7 cc CO_2 = 46.1% CO_2

5.5 cc CO = 53.9% CO

Lb. carbon converted to CO_2 and CO
0.0439 X .461 = 0.0202 lb. C to CO
0.0439 X .539 = 0.0237 lb. C to CO_2

Lb. mols carbon converted to CO_2 and CO

$0.0202 \text{ lb. C} \times \frac{lb. \text{ mol C}}{12 \text{ lb. C}} = 0.001685$ lb. mols C to CO_2

$\frac{0.0237}{12} = 0.00197$ lb. mols C to CO

$C + 2H_2O \longrightarrow CO_2 + 2H_2$
$C + H_2O \longrightarrow CO^2 + H_2^2$
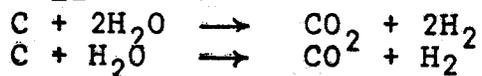
Lb. mols Hydrogen for 0.001685 mols C to CO_2 =
2 X 0.001685   = 0.00338
Lb. mols Hydrogen for 0.00197 mols C to CO =
1 X 0.00197   = 0.00197
           0.00535 lb. mols H.

1 mol gas = 379.5 cu.ft. @ 60°F and 1 atm.
1 mol gas = 379.5 cu.ft. $\times \frac{760 \text{ mm Hg}}{745.2 \text{ mm Hg}} \times \frac{540°R}{520°R} =$ 403 cu.ft.
@ 80°F
and 745.2
mm Hg.

(Assume CO_2, H_2 and CO are ideal gases @ 80° F and 745.2 mm Hg.)

Total Gas Volume
$\frac{403 \text{ ft.}^3}{mol} \times 0.00165$ mol = 0.68 ft^3 CO_2
403   X 0.00197   = 0.79 ft^3 CO
403   X 0.00535   = 2.16 Ft^3 H_2
     Total Gas Volume   3.63 Ft^3

Gas metered 4.05 Ft^3 wet basis Table 5

Metered Gas Volume - dry basis

$$4.05 \times \frac{(745.2 - 26.3)}{745.2} = 3.91 \text{ Ft}^3 \text{ dry basis}$$

Correction of Metered Gas Volume for CO_2, H_2 and CO content only-dry basis $= 3.91 \times (1.00 - \frac{4.2}{31.9}) = 3.39 \text{ Ft}^3$ dry basis

Per Cent error $\frac{3.63 - 3.39}{3.63} \times 100 = 6.6\%$ or 7%

APPENDIX III

LITERATURE SEARCH

The following Indicies were searched.

TITLE	YEARS
Chemical Abstracts	1920 - 1967
Engineering Index	1900 - 1967
Industrial Arts and Applied Technology Index	1913 - 1967
Uniterm Index	1956 - 1966

Some of the applicable headings were as follows:

Carbon - activated

Coke

Petroleum Coke

The Bibliography of Solid Adsorbents, written by V. R. Dietz, and published by the National Bureau of Standards 1944, was also used. Most of the articles were found in the Industrial Engineering and Chemistry and Chemical Engineering journals. Bibliographies of various journal articles were also examined.