ACTIVATION OF PETROLEUM COKE

by

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ABSTRACT

The aim of this research was to determine:

a. Whether an activated carbon could be made from petroleum coke

b. How would the activated coke's quality (decolorization and water purification ability) compare with that of commercial carbons.

The author obtained an intermediate quality activated carbon by passing steam through a bed of petroleum coke wetted with phosphoric acid. Activation experiments were made at 1550°F in which the particle size of the coke sample and the steam flow rate were varied. In a modified process, the coke was boiled with phosphoric acid before phosphoric acid-steam activation. The product was of the same quality as that obtained by the phosphoric acid-steam process. Activation was also attempted by using a stagewise procedure, i. e. the treated coke obtained above was mixed with phosphoric acid and again steam activated. This method did not give a higher activation.

In a modified process steam was passed through a bed of coke wetted with a mixture of phosphoric and sulfuric acids (rather than phosphoric acid alone). The method gave approximately the same activation as with phosphoric acid. It would be more economical to use a mixture of phosphoric and sulfuric acids rather than phosphoric acid alone.

In another method of activation an alkali was used instead of an acid. Activation was attempted by treating the coke with steam, roasting

the product with caustic soda, and again treating the coke with steam. This method was not successful.

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CHAPTER ONE

INTRODUCTION

In a meeting held in the summer of 1966, representatives of the Kansas State Geological Survey, the Chemical and Petroleum Engineering Department of the University of Kansas, the Economics Department of Wichita State University, and the city of El Dorado, Kansas, decided to initiate a program of industrial development using the region's raw materials and business and technical knowhow. The project chosen was the production of activated carbon from petroleum coke produced at Skelly Oil Company's refinery in El Dorado[12].

The economic study of the project was made by Wichita State University. It indicated a market for decolorizing and water purification carbons[12].

The aim of this research was to determine:

a. Whether an activated carbon could be made from petroleum coke.

b. How would the activated coke's quality (decolorization and water purification ability) compare with that of commercial carbons.

Mr. Carl Vickburg, a graduate student in Chemical Engineering at Kansas University, did the initial work on the development of an activated carbon for use in the aforesaid fields. This author continued the work.

CHAPTER TWO

LITERATURE SURVEY

2.1 General

The earliest application of carbon as an adsorbent is attributed to Scheele who conducted experiments on gases exposed to carbon in 1773[3]. Wood charcoal was used in the decolorization of raw sugar by an English refinery as early as 1794[4]. In 1811 Figuier published a memoir stating that bone char was a superior decolorizing agent than the existing vegetable charcoal. During the nineteenth century activated carbon was prepared from a number of other sources such as peat, paper wastes, coconuts, and blood.

In 1900 and 1901 Ostrejko patented activation processes which are the basis of manufacture of a large number of modern activated carbons. One of the processes is the carbonization of a mixture of vegetable matter and metallic chlorides. In another patent Ostrejko suggests activation of vegetable charcoal by oxidation with carbon dioxide at a suitable temperature[3,4].

World War I provided an impetus to the development of the activated carbon industry. The use of chlorine by the Germans in 1915 necessitated the production of an adsorbent suitable for use in gas masks.

The important markets for activated carbon include sugar decolorization, water purification, gas adsorption, dry cleaning, pharmaceuticals, and plasticizers[3].

The raw materials for manufacture of activated carbon include bituminous coal, coconut shells, wood, peat, lignite, pulp mill black-ash and petroleum base residues[3].

2.2. Principles of Activation

It is not clear what happens during activation aside from the fact that there is an increase in surface area and a porous structure is developed. The combination of steps to be employed in activating a carbon depend upon the nature of the raw material and the specific properties desired in the carbon. The optimum conditions for each step depend upon the preceding steps which leave an imprint on the carbon. Hassler describes this by saying that "carbon has a memory"[3].

The nature of the activated carbon produced is dependent upon:

a. Raw material
b. Carbonization
c. Oxidation

A discussion of these items follows.

a. Raw Material. The nature of the activated carbon depends strongly upon the raw material. Materials that contain mineral ingredients (e. g. bones) are ideal for making decolorizing carbons. Substances such as wood, which are essentially free of minerals, can give a decolorizing carbon if mixed with metallic chlorides before carbonizing[3]. However, activated carbon produced from wood pulp is not hard enough for use as a gas adsorbent. A tough, fibrous material like coconut shells is an excellent raw material for gas adsorbing carbons. Highly dense materials like petroleum base by-products are more suitable for water-purification than as decolorizers[12].

b. Carbonization. Temperature is the critical factor in carbonization. This was made clear by Chaney, in 1919, in a paper outlining the nature of active carbon[1,2,5]. According to him "elementary carbon (other than diamond and graphite) exists in two modifications 'active' and 'inactive'". In the process of distillation of carbonaceous materials, at high temperatures (above 500 to 700°C) inactive carbon is formed by the decomposition of the unstable hydrocarbons. At lower temperatures (below 500 to 700°C) the unstable hydrocarbons decompose forming active carbon. The active carbon adsorbs some of the hydrocarbons. This adsorption complex is very stable, and the hydrocarbons are retained by the active carbon even at very high temperatures. The carbonization temperature should be such that inactive carbon is not formed. For most materials the upper temperature limit is around 600°C.

The presence of mineral salts and other non-carbon elements enhances the adsorptive powers of carbon[3,4]. However, the mechanism is not clear. One view is that "the mineral ingredients provide a skeleton on which the carbon is deposited - the carbon being bonded by adsorption forces to the mineral elements. When the mineral ingredients are subsequently dissolved by acid, or water, the exposed carbon becomes free to attract other substances"[3]. It has been observed that the yield of char is increased if dehydrating salts like zinc chloride are added to the raw material being carbonized. The zinc chloride causes the hydrogen and oxygen to be stripped away as water rather than as hydrocarbons.

c. Oxidation. The carbonized char is usually oxidized. Steam air and carbon dioxide are some of the commonly used oxidation agents[3]. Phosphoric acid is sometimes used for oxidation[3,7,11]. Some activation is due to the dehydrating power of phosphoric acid.

According to Chaney, the hydrocarbons adsorbed during the carbonization process are preferentially oxidized in the oxidation process. This leaves the carbon surface free to attract and adsorb other substances [1,2,5]. Chaney's theory accounts for the general improvement in adsorptive power but does not explain differences in specific adsorptive power, e. g. oxidation with steam at 800°C provides adsorptive powers different from those produced by oxidation with air at 400°C.

The adsorptive powers obtained by oxidation are determined by:

(i) chemical nature and concentration of the oxidizing agent
(ii) temperature of reaction
(iii) extent to which the reaction is conducted (percent recovery of carbon)
(iv) nature and concentration of mineral and non-carbon ingredients in the carbon.

The presence of some non-carbon substances has been found to be helpful in the oxidation process. Two of the possible mechanisms are:

(1) Oxidation occurs at the bonds between carbon and non-carbon atoms leaving the carbon free to adsorb other substances.

(2) Berl found evidence that "some elements, such as potassium, can penetrate between the hexagon plates of crystallites and spread them apart, enabling erosion to occur at surfaces otherwise unexposed"[3]. (Amorphous carbons like coke and activated carbons are composed of submicroscopic crystals, called "crystallites". X-ray studies have shown that amorphous carbons consist of flat plates in which the carbon atoms are arranged in a hexagonal lattice. Each carbon atom is held by covalent bonds to three other carbon atoms except for carbon atoms on the edges. Crystallites are formed by two or more of these plates being stacked one above the other).

The specific adsorptive capacities of an adsorbent do not develop at a uniform rate, i.e. in general, adsorptive capacity for iodine develops during the initial period and then ceases to increase further; but, adsorptive capacity for molasses color develops only during the later stages of activation.

An alkali activated carbon can be obtained by heating a mixture of carbonized material and caustic at temperatures above 500°C[3,8].

2.3. Literature on Activation of Petroleum Coke

There is not much published literature on activation of petroleum coke besides some patents. The earlier patents[9] (pre 1950) suggested the passing of steam/flue gases/air/hydrocarbon vapors through a bed of

(i) petroleum coke

or

(ii) a mixture of coke and acid

or

(iii) a mixture of coke and a sulfur containing compound like potassium sulfide or sulfuric acid

at atmospheric/superatmospheric/subatmospheric pressures and high temperatures.

Most of the patents[10] granted in the 1950's suggested carbonization of liquid petroleum by-products (or its mixture with chemicals), and oxidizing the carbonized material.

2.4. Vickburg's Work on Activation of Petroleum Coke

Vickburg[12] attempted to "activate the petroleum coke by passing superheated steam through the coke bed. The reaction temperature was approximately 800-900°C. Isothermal tests were conducted through the range to determine the optimum operating temperature (found to be 1550°F). In a modified process, activation of the carbon was attempted by wetting the coke with phosphoric acid before introducing superheated steam.

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

The laboratory tests employed for evaluation of the treated coke as an activated carbon were the molasses test and the iodine test.

The results of the molasses test indicate that the carbons produced have little or no decolorization 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. Commercial carbons tested adsorbed 55% to 95% of the iodine stock solution".

It was observed that Vickburg did not grind the carbons to the same size before analysis - the standard carbons were finer than Vickburg's coke. The treated coke obtained by Vickburg from the phosphoric acid-steam process and the standard carbons were ground, and the fractions finer than 200 mesh analyzed. Vickburg's treated coke was found to be intermediate in activation capacity to the two standard carbons. In view of this development it was decided to concentrate on optimization of a phosphoric acid-steam activation process.

CHAPTER THREE

METHOD FOR ACTIVATION OF PETROLEUM COKE

As mentioned in the last chapter, Vickburg's results of the phosphoric acid-steam activation process were encouraging, and it was decided to concentrate on the optimization of this process. The coke-phosphoric acid samples were treated with superheated steam at 1550°F (the optimum temperature found by Vickburg). The particle size of coke and the flow rate of steam were varied to determine the optimum operating conditions.

In a modified process an attempt was made to activate the coke by passing steam through a bed of coke wetted with a mixture of sulfuric and phosphoric acids. It was thought that use of sulfuric acid might result in better activation as it is stronger than phosphoric acid. Besides, it would be more economical to use a mixture of sulfuric and phosphoric acids rather than phosphoric acid alone.

An attempt was also made to activate the coke by a stagewise process of steam activating it, roasting with alkali and further steam activation. This method was successfully used in the activation of anthracite coal[3]. Details of the experimental procedure are given in Section 3 of this chapter.

3.1. Phosphoric Acid-Steam Activation

In this process coke wetted with phosphoric acid is subjected to

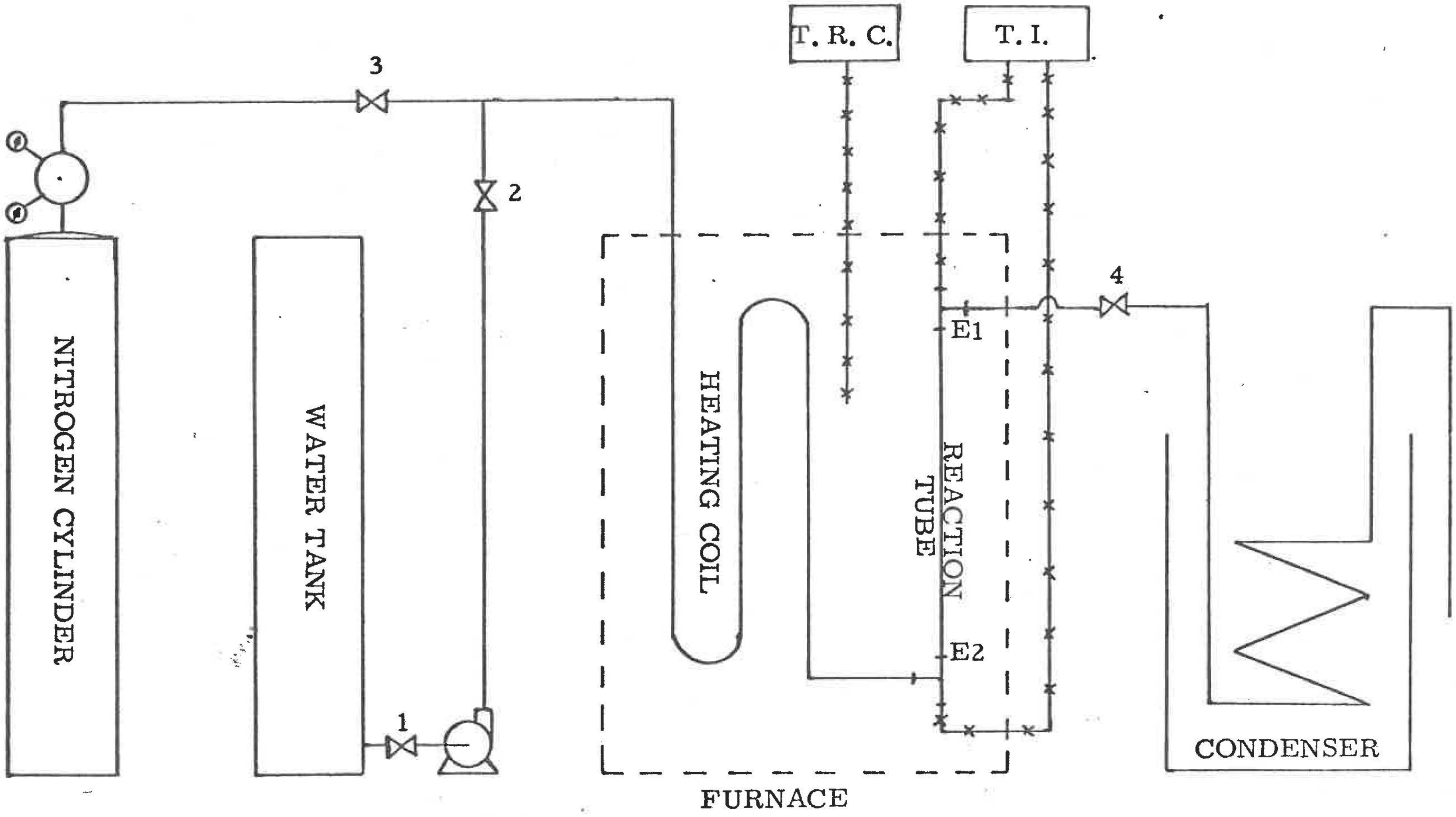

Figure 3. 1 Flow Diagram of the Phosphoric Acid-Steam Activation Process

steam treatment. It was decided to optimize the process by treating the coke-phosphoric acid samples with superheated steam at 1550°F (the optimum temperature found by Vickburg) and varying the particle size of coke and the flow rate of steam. In case diffusion through the pores offered the controlling resistance a decrease in particle size should increase the adsorptive capacity of the petroleum coke. The operating conditions are given in Table 3.1 (Run Nos. 1,4,5,6 and 7).

It was thought that boiling with phosphoric acid might be helpful. The petroleum coke was boiled in phosphoric acid, washed with water and dried and a mixture of the dried coke and phosphoric acid treated with steam (see Table 3.1, Run Nos. 2 and 3).

It was felt that the phosphoric acid was consumed and/or carried away by the steam in the early stages of the reaction. So activation was also attempted by using a stagewise procedure, i. e. the treated coke obtained above was wetted with phosphoric acid and again steam activated. The operating conditions are given in Table 3.1 (Run Nos. 5 and 8).

3.1.1. Description of the Process. Coke wetted with phosphoric acid was placed in the reaction tube (see Fig. 3.1). Nitrogen at 5 psig. provided the inert atmosphere in the reaction tube. The furnace was switched on and the temperature controlled by the furnace temperature recorder and controller. When a temperature of 1550°F was attained the nitrogen supply was switched off and the metering pump started to provide a metered rate of water to the heating tube. The superheated steam formed in the heating tube flowed through the reaction tube. The reaction products flowed through the condenser where steam was condensed and the noncondensables vented to the atmosphere.

3.1.2. Description of the Equipment.

Heating Coil

The heating coil consisted of a 9 ft. coil of 1 in., schedule 40 stainless steel 316 pipe packed with 3/16 in. x 1/4 in alumina cylinders.

Reaction Tube

A 1 in., schedule 40 stainless steel 316 pipe of length 16 ins. was used. The reaction tube corroded quite fast under the severe operating conditions and had to be replaced often. A Hastelloy B tube was used for sometime but it also corroded appreciably and it was found more economical to use stainless steel 316 tubes and replace them as required.

Thermocouple Probes

The thermocouple probes were made from 14 gauge Chromel-Alumel (type K) wire and were protected with ceramic insulators. They were housed in stainless steel wells (I. D. = 0.269 in., O. D. = 0.465 in., L = 5 in.) welded into 1 in. elbows (E1 and E2 in Fig. 3.1).

The probes and potentiometer were standardized by placing the probes in the furnace and comparing their temperatures with those obtained by a standard probe and potentiometer. The readings agreed within ± 5°F in the operating temperature range.

Furnace

A Harper electric furnace (Model HS 101013 P 32) was used. The specifications were: 180 volts, 20 KW, and maximum operating temperature of 2900°F.

Metering Pump

A Zenith metering pump with a maximum capacity of 100 ml/min was used.

3.1.3. Description of Process Operation.

General. Petroleum coke wetted with phosphoric acid was packed in the reaction tube and held in position by 200 mesh stainless steel screen supports. A one inch packed bed of opaline sandstone (contains mainly quartz) was provided on both ends of the coke bed. The reaction tube was then connected to the heater section and exit pipe. All connections were threaded and a lubricant was used to prevent freezing of the pipe threads.

At 1550°F it was found that the temperature at the top of the reaction tube was about 40°F higher than the temperature at the lower end. It was also observed that the temperature recorded by the furnace T. R. C. was always about 50°F less than that given by a thermocouple probe placed next to the furnace probe (fixed in the middle of the furnace).

This difference in temperature was due to error in the furnace recorder. So, the furnace T. R. C. was set at 1500°F to make runs at 1550°F. The furnace T. R. C. could maintain the temperature within ± 10°F of the desired temperature (1550°F).

Plant Operating Procedure. The procedure was as follows:

1. Valves 4 and 3 were opened and nitrogen pressure regulators set at 5 psig. discharge pressure.
2. The furnace T. R. C. was set at 1500°F.
3. The furnace transformer was turned on.
4. When the operating temperature was attained, valve 3 was closed.
5. Valves 2 and 1 were opened and the metering pump (preset at desired flow rate) was switched on.
6. After the desired activation time the pump was shut off and valve 2 was closed.
7. Valve 3 was opened and nitrogen at 5 psig. discharge pressure passed through reaction bed to prevent burning of coke.
8. Transformer switched off.
9. When a temperature of about 800°F was reached, the nitrogen supply was switched off.
10. The furnace was allowed to cool for 8-10 hours.

3.1.4. Recovery of Treated Coke. The reaction tube and heating coil assembly was removed from the furnace and the reaction tube disconnected. The coke usually contained some iron compounds. A magnet was used to remove the magnetic impurities. The coke was then sieved through a 150 mesh screen. It was found that most of the impurities were finer than 150 mesh and negligible amount of coke was so fine. The coke was then weighed and stored.

3.2. Phosphoric Acid-Sulfuric Acid-Steam Activation

A run was made by steam activating coke wetted with phosphoric and sulfuric acids. The activation procedure was the same as for phosphoric acid-steam activation procedure (see Table 3.1, Run No. 12).

3.3. Alkali Activation

The procedure was:

1. 125 gm. of petroleum coke steam activated for half hour at 1550°F. Steam flow rate was 15 ml. (liquid water) per minute. The product was weighed.
2. 90 gm. of coke obtained in step 1 was mixed with 20 gm. of NaOH (dissolved in 50 ml. of water). The mixture was dried and then roasted at 1600°F for 15 min. in open ceramic pans. The product was washed with water and agitated with water for 15 hours. Then it was washed with diluted sulfuric acid and water. The product was dried and weighed.
3. 50 gm. of coke obtained in step 2 was steam activated at 1550°F for 15 minutes. Steam flow rate was 15 ml. (liquid water) per minute. See Table 3.1, Run Nos. 9,10 and 11.

TABLE 3.1

OPERATING CONDITIONS FOR VARIOUS PROCESSES

Process	Run No.	Coke Size Tyler Mesh	Steam Flow Rate, ml/min	Remarks
Phosphoric Acid-Steam Activation	1	8-16	15	100 gm. of coke wetted with 20 ml. of 85% phos. acid was steam activated for 3 hrs.
	Vickburg No. 18	8-16	18	64.1 gm. of coke wetted with 10 ml. of 85% phos. acid was steam activated for 1.5 hrs.
	Vickburg No. 19	8-16	9	64.1 gm. of coke wetted with 10 ml. of 55% phos. acid was steam activated for 3 hrs.
	4	20-60	15	100 gm. of coke wetted with 20 ml. of 85% phos. acid was steam activated for 1.5 hrs.
	7	20-60	15	100 gm. of coke wetted with 20 ml. of 85% phos. acid was steam activated for 3 hrs.

TABLE 3.1 (continued)

Process	Run No.	Coke Size Tyler Mesh	Steam Flow Rate, ml/min	Remarks
Phosphoric Acid-Steam Activation	6	20-60	7.5	100 gm. of coke wetted with 20 ml. of 85% phos. acid was steam activated. The actual time for steam activation is unknown as steam valve got clogged while conducting experiment.
Phosphoric Acid-Steam Activation 2-Stage	5	20-60	15	100 gm. of coke wetted with 20 ml. of 85% phos. acid was steam activated for 1 hr.
	8	less than 20	15	50 gm. of coke from run no. 5 wetted with 10 ml. of 85% phos. acid was steam activated for half hour.
Phosphoric Acid-Steam Activation Preceded by Boiling with Phosphoric Acid	2	8-16		Coke boiled with phos. acid.
	3	less than 8	15	100 gm. of coke from run no. 2 wetted with 20 ml. of 85% phos. acid was steam activated for 3 hrs.

TABLE 3.1 (continued)

Process	Run No.	Coke Size Tyler Mesh	Steam Flow Rate, ml/min	Remarks
Phosphoric Acid-Sulfuric Acid-Steam Activation	12	20-60	15	100 gm. of coke wetted with 10 ml. of 85% phos. acid and 10 ml. of conc. sulfuric acid was steam activated for 2 hrs.
Alkali Activation	9	20-60	15	125 gm. of coke steam activated for 0.5 hr.
	10	less than 20		90 gm. of coke from run no. 9 was mixed with 20 gm. of NaOH (dissolved in 50 ml. of water). Dried. Product roasted at 1600°F for 15 mins. Washed with water, agitated with water for 15 hrs. Washed with diluted sulfuric acid, dried.
	11	less than 20	15	50 gm. of coke from run no. 10 steam activated for 0.5 hr.

CHAPTER FOUR

TESTING OF TREATED COKE

The tests selected for evaluation of the adsorption power of the treated coke were the iodine-adsorption test and the molasses test. These tests are widely used by industry, are inexpensive, and could be performed with the available laboratory equipment.

The use of the molasses test for evaluating carbon is quite common with sugar refiners as it gives a close indication of the actual results that can be obtained. The test has a limitation because molasses obtained from different sources vary in depth of color and type of color bodies. Thus, the results obtained with one molasses cannot be compared with those obtained from a different molasses. So it is necessary to compare the molasses value of the carbon with that of a reference carbon[4].

In the molasses test a measured amount of the molasses solution and a fixed amount of coke sample are mixed for a fixed time and filtered. The percent light transmittance of the filtrate is measured by a spectrophotometer using distilled water as a standard.

It has been observed that the iodine test gives a good indication of the ability of a carbon to remove taste and odor. The test is a safe criteria for evaluating the petroleum coke's capacity as a water purification carbon[3].

In the iodine test a measured amount of the iodine solution and a fixed amount of coke sample are mixed for a fixed time and filtered. The filtrate is titrated against sodium thiosulfate solution, and the percent iodine removed is calculated.

The molasses and iodine tests complement each other. The molasses test gives an indication of the macropore structure of the carbon (100 angstroms or larger) while the iodine test offers a qualitative idea of the 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[3,12].

It would be advisable to measure the surface area of the activated carbon. Unfortunately, the testing equipment was not available.

Details of the iodine-adsorption test and molasses test are given in Appendix I.

CHAPTER FIVE

RESULTS

The activation processes investigated in this research are:

1. Phosphoric acid-steam activation (Run Nos. 1,4,5,6,7,V18 and V19)
2. Stagewise phosphoric acid-steam activation (Run Nos. 5 and 8)
3. Phosphoric acid-steam activation preceded by boiling with phosphoric acid (Run Nos. 2 and 3)
4. Phosphoric acid-sulfuric acid-steam activation (Run No. 12)
5. Alkali activation (Run Nos. 9,10 and 11)

As stated previously, the iodine adsorption test was performed to evaluate the coke's capacity as a water purification carbon. The test gives a good indication of the ability of an activated carbon to remove taste and odor. It is an indicator of the micro-pore structure. The molasses test was used to evaluate the decolorization ability of the treated coke. The molasses test is an indicator of the macro-pore structure.

5.1. Iodine Adsorption Test

The results of the iodine adsorption test along with the process conditions are listed in Table 5.1. Figure 5.1 is a plot of per cent iodine removed against per cent weight loss of coke. Results for all the processes have been plotted on the graph for comparison purposes. Results obtained with the original coke and commercial carbons are also shown. A curve has been drawn through points representing runs made for the phosphoric acid-steam activation process using 20-60 mesh coke and a steam flow rate of 15 ml/min (Run Nos. 4,5 and 7). The curve has been extended to point O which represents the per cent iodine removed by the original petroleum coke.

5.2. Molasses Test

Data for the molasses test is listed in Table 5.1. Figure 5.2 is a plot of per cent light transmittance against per cent weight loss of coke. Test data for all the processes, original coke, and commercial carbons have been plotted. Distilled water was used as the standard for light transmittance.

A curve has been drawn through points 4 and 7 which represent runs made for the phosphoric acid-steam activation process using 20-60 mesh coke and a steam flow rate of 15 ml/min. The curve has been extrapolated to 0% weight loss of coke. It intersects the ordinate above point M since the per cent light transmitted through molasses solution treated with original coke is higher than the per cent light transmitted through the molasses stock solution.

The molasses test results for the original coke and runs 5 and 6 are in error because, by mistake, the spectrophotometer was calibrated with air as a standard (rather than water). The test was not repeated for these runs as the molasses solution had become turbid by the time this error was observed, and it would have meant repeating the test for all the runs if a new molasses solution were made.

5.3. Discussion of Results

The results of the phosphoric acid-steam activation process (Figures 5.1 and 5.2) show that an intermediate quality activated carbon can be obtained. The iodine adsorption test and the molasses test were repeated for runs 1 and 3 and for the standard carbons. The tests were reproducible within ± 6 per cent (Table A.5). All the runs were made at 1550°F (the optimum temperature determined by Vickburg).

A decrease in particle size apparently gave a slightly higher per cent removal of iodine. From Figure 5.1 it is seen that the per cent iodine removed is slightly higher for 20-60 mesh coke than that for 8-16 mesh coke (Run Nos. 1, V18, and V19). A further decrease in particle size (below 60 mesh) is not recommended since it would create recovery problems and a high pressure drop when the activated coke is used in an adsorber.

The results of the molasses test (Figure 5.2) show no improvement in the decolorization ability of the coke by decreasing the particle size. The molasses test result for Vickburg's Run No. 18 did not come out as expected. The per cent light transmittance for Vickburg's 8-16 mesh coke was slightly higher than that for 20-60 mesh coke. This discrepancy cannot be well explained. Maybe the aging of Vickburg's coke enhanced its adsorptive capacity for molasses color. Hassler[3] has reported instances of increase of specific adsorptive powers of coke with age.

In the range of steam flow rates studied in this research, a decrease in steam rate did not give any significant increase in the adsorption capacity of the coke. From Figures 5.1 and 5.2 it is seen that the activated carbons obtained by using steam flow rates of 7.5 ml/min (Run No. 6) and 15 ml/min were of the same quality. All the remaining runs were made at 15 ml/min as it was difficult to adjust the steam flow rate to 7.5 ml/min.

Some patents suggest the boiling of coke with phosphoric acid[8]. However, the results of Run No. 3 show that the boiling of coke in acid was not helpful.

It was felt that the phosphoric acid was consumed and/or carried away by the steam in the early stages of the reaction so activation was also attempted by using a stagewise procedure, i. e. the treated coke obtained above was wetted with phosphoric acid and again steam activated (Run Nos. 5 and 8). Test results show that this two-stage activation process did not give a better activated carbon than the single stage process. It appears that the second application of phosphoric acid is not helpful as the liquid phosphoric acid errodes away the highly active carbon near the particle surface before the furnace becomes hot enough for the acid to vaporize.

The use of sulfuric acid in addition to phosphoric acid (Run No. 12) gave approximately the same activation as with phosphoric acid. Using a mixture of phosphoric and sulfuric acids would be more economical as sulfuric acid is cheaper than phosphoric acid.

In another method of activation, an alkali was used instead of an acid. Activation was attempted by treating the coke with steam, roasting the product with caustic soda, and again treating the coke with steam (Run Nos. 9,10 and 11). The method was unsuccessful.

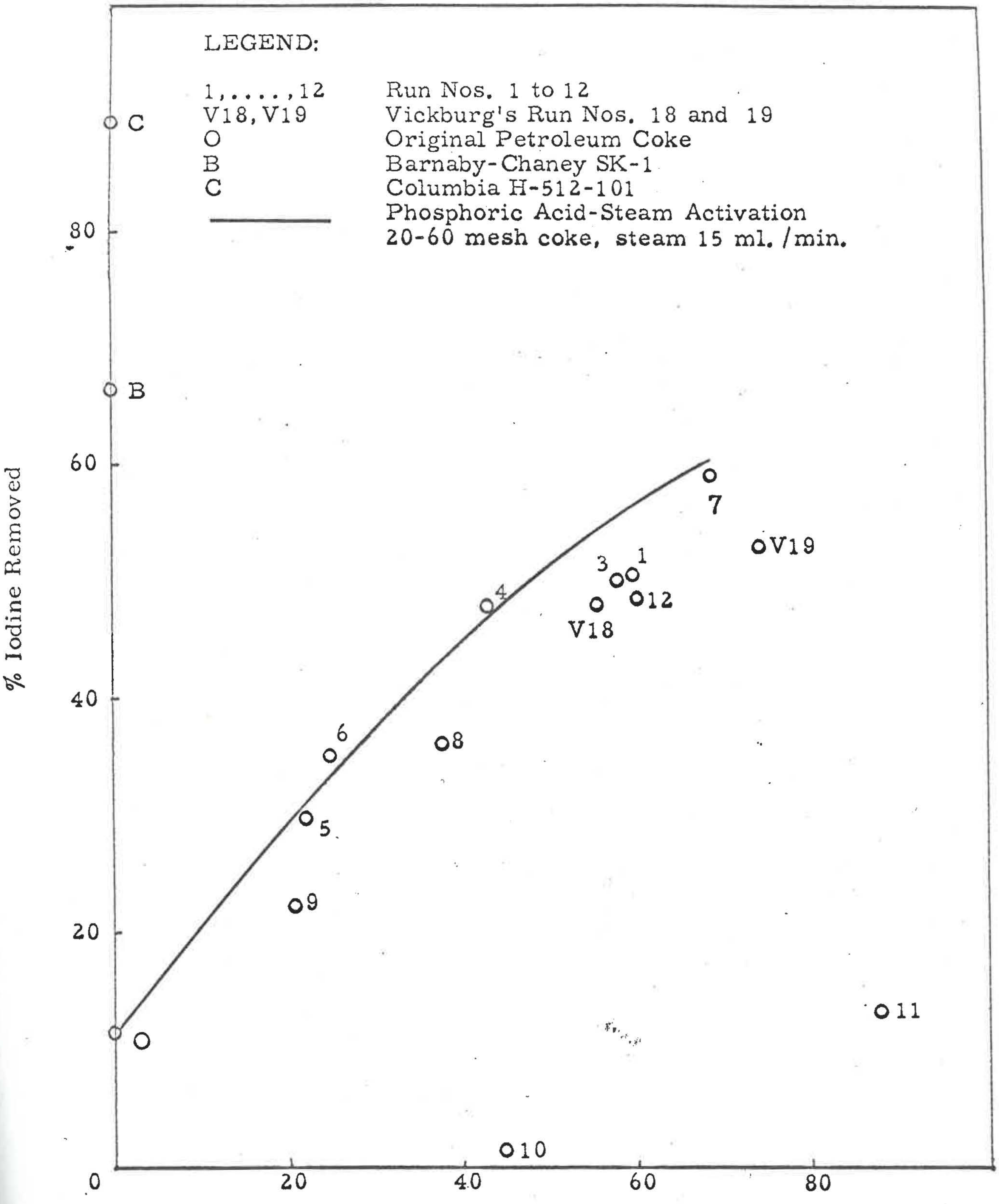

Figure 5.1 Development of Adsorption Capacity of Coke for Iodine with Weight Loss of Coke

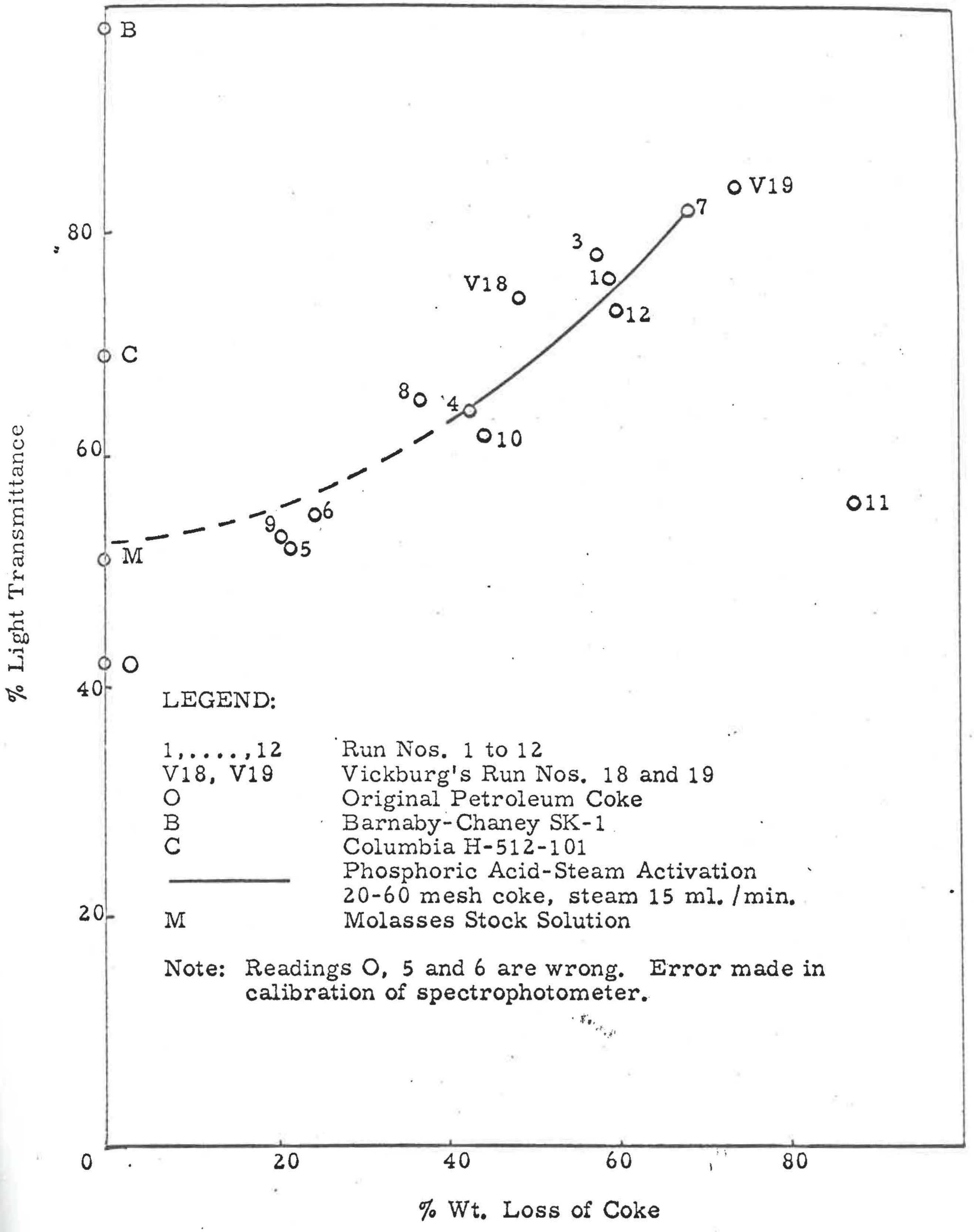

Figure 5.2 Development of Adsorption Capacity of Coke for Molasses Color with Weight Loss of Coke

TABLE 5.1

RESULTS OF IODINE ADSORPTION TEST AND MOLASSES TEST

Run No.	Coke Size Tyler Mesh	Steam Flow Rate, ml/min	% Iodine Removed	% Light Transmittance	% Wt. Loss of Coke	Remarks
Original Coke			11.6	42*		
Columbia H-512-101			89.7	69		
Barnaby Chaney SK-1			66.5	98		
1	8-16	15	50.4	76	59.7	100 gm. of coke wetted with 20 ml. of 85% phos. acid was steam activated for 3 hrs.
2	8-16					Coke boiled with phos. acid
3	less than 8	15	50.1	78	58.4	100 gm. of coke from run no. 2 wetted with 20 ml. of 85% phos. acid was steam activated for 3 hrs.
4	20-60	15	48.0	64	43	100 gm. of coke wetted with 20 ml. of 85% phos. acid was steam activated for 1.5 hrs.

TABLE 5.1 (continued)

Run No.	Coke Size Tyler Mesh	Steam Flow Rate, ml/min	% Iodine Removed	% Light Transmittance	% Wt. Loss of Coke	Remarks
5	20-60	15	29.7	52*	22	100 gm. of coke wetted with 20 ml. of 85% phos. acid was steam activated for 1 hr.
6	20-60	7.5 (approx)	35.1	55*	25	100 gm. of coke wetted with 20 ml. of 85% phos. acid was steam activated. The actual time for steam activation is unknown as steam valve got clogged while conducting experiment.
7	20-60	15	59.2	82	69	100 gm. of coke wetted with 20 ml. of 85% phos. acid was steam activated for 3 hrs.
8	less than 20	15	36.3	65	37.9	50 gm. of coke from run no. 5 wetted with 10 ml. of 85% phos. acid was steam activated for half hour.
Vickburg No. 18	8-16	18	48	74	55.7	64.1 gm. of coke wetted with 10 ml. of 85% phos. acid was steam activated for 1.5 hrs.

TABLE 5.1 (continued)

Run No.	Coke Size Tyler Mesh	Steam Flow Rate, ml/min	% Iodine Removed	% Light Transmittance	% Wt. Loss of Coke	Remarks
Vickburg No. 19	8-16	9	53	84	74.4	64.1 gm. of coke wetted with 10 ml. of 55% phos. acid was steam activated for three hrs.
9	20-60	15	22.4	53	21	125 gm. of coke steam activated for 0.5 hr.
10	less than 20		1.75	62	45	90 gm. of coke from run no. 9 was mixed with 20 gm. of NaOH (dissolved in 50 ml. of water). Dried. Product roasted at 1600°F for 15 mins. Washed with water, agitated with water for 15 hrs. Washed with diluted sulfuric acid, dried.
11	less than 20	15	13.1	56	88	50 gm. of coke from run no. 10 steam activated for 0.5 hr.
12	20-60	15	48.8	73**	60.2	100 gm. of coke wetted with 10 ml. of 85% phos. acid and 10 ml. of conc. sulfuric acid was steam activated for 2 hrs.

* % light transmittance value is wrong because of an error in calibration of the spectrophotometer.

** Molasses solution was turbid. Reading may be inaccurate.

Note: Light transmittance value of molasses stock solution was 51.

CHAPTER SIX

CONCLUSIONS AND RECOMMENDATIONS

6.1. Conclusions

The test results show that an intermediate quality activated carbon can be obtained by the phosphoric acid-steam activation process (or by phosphoric acid-sulfuric acid-steam activation process). The use of sulfuric acid in addition to phosphoric acid gave approximately the same activation as with phosphoric acid. Using a mixture of phosphoric and sulfuric acids would be more economical as sulfuric acid is cheaper than phosphoric acid. For 31% carbon recovery an iodine removal of 59% and 82% transmittance of light were obtained in comparison to 67% to 90% iodine removal and 69% to 98% light transmittance for commercial carbon. From the trend of the graphs it is seen that for 10% carbon recovery a carbon with 65% iodine removal and 90% light transmittance capacity can be obtained. With a cheap material like petroleum coke it may be economical to go up to 90% carbon loss (10% carbon recovery).

6.2. Recommendations

It is felt that further study should be done and that the starting material should be the liquid feed to the coking unit of Skelly Refinery. Phosphoric acid, sulfuric acid, and/or metallic chlorides, carbonates or sulfates should be added to the liquid before carbonizing and subse-steam activation. The phosphoric acid might produce a more porous coke because gases would tend to flow out of the coke mass. This porous coke would offer less resistance to the diffusion of steam during the steam activation stage. The presence of metallic chlorides during carbonization has been found to increase activation though the theory is not clear. The possible mechanisms are discussed in Chapter 2.

In case it is not feasible to add chemicals to the liquid feed to the coking unit of the Skelly Refinery (presence of acid in the overhead product of the coking unit may be undesirable and the acid may corrode the existing coking equipment), the following scheme is recommended.

(1) Pulverize the petroleum coke
(2) Make briquets after mixing the coke with a binder, phosphoric acid, and/or sulfuric acid
(3) Carbonize the briquets by heating the reaction tube to 1550°F
(4) Pass steam through the reaction tube.

LITERATURE CITED

1. Chaney, N.K., Trans. Electrochem. Soc., 3:91 (1919).
2. Chaney, N.K., A.B. Ray and A. St. John, Ind. Eng. Chem., 15, 1244 (1923).
3. Hassler, J.W., Activated Carbon, Chemical Publishing Co., Inc., New York (1963).
4. Mantell, C.L., Adsorption, McGraw-Hill Book Co., Inc., New York (1951).
5. Ray, A.B., Chem. and Met. Eng., 28, 977 (1923).
6. Treadwell, F.P. and W.T. Hall, Analytic Chemistry, 2:583, John Wiley and Sons, Inc., New York (1946).
7. U.S. Patents 1610399, 1659931, 1689647.
8. U.S. Patents 1588868, 1704765, 1251546, 2067985, 2216756.
9. U.S. Patents 1763101, 1763102, 1819314, 1903834, 2342862.
10. U.S. Patents 1925438, 2718505.
11. U.S. Patent 1438113.
12. Vickburg, C.D., M.S. Thesis, University of Kansas (1968).

APPENDIX I

TEST PROCEDURES

The test procedure for the Iodine Adsorption Test and the Molasses Test was essentially the same as used by Vickburg. The only modification was that the coke was ground and the fraction finer than 200 mesh was used for analysis.

A. Iodine Adsorption Test

The test is based on the fundamental iodimetric reaction:

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

Iodine solution is added to the coke sample and the mixture is stirred. It is then filtered and the amount of iodine adsorbed can be calculated by titrating the filtrate with sodium thiosulfate solution. The reaction is very sensitive and finds a wide application in analytical chemistry.

1. Reagents

Iodine Solution	25.4 ± 0.1 gm. Iodine per liter dissolved with 38 gm. potassium iodide per liter in water
Sodium Thiosulfate Solution	25 gm. of $Na_2S_2O_3 \cdot 5H_2O$ per liter in water

Starch Solution	2.5 gm. of starch added to a liter of boiling water. Preserved by addition of 1 ml. of chloroform.

2. Procedure

   (i) Grind the dry carbon, weigh 1.0 gm. of the fraction finer than 200 mesh, and place it in a 200 ml. Erlen~~men~~meyer Flask.

   (ii) Add 50 ml. iodine solution.

   (iii) Swirl to wet carbon and swirl for one additional minute.

   (iv) Filter immediately through a No. 2V fluted Whatman filter paper.

   (v) Pipette 25 ml. of filtrate into a 150 ml. beaker, and titrate with N/10 Sodium Thiosulfate solution.

3. Evaluation of % Iodine Removed

$$\%\text{ of iodine removed} = \frac{\text{Normality of Iodine Stock Solution} - \text{Normality of Treated Solution}}{\text{Normality of Iodine Stock Solution}} \times 100$$

4. Standardization of Stock Solutions

   (i) Standardization of Sodium Thiosulfate Solution

   "The reaction between potassium dichromate and potassium iodide can also be used for the standardization of sodium thiosulfate solution; the dichromate is reduced to green salts and an equivalent weight of iodine being set free provided that the solution is 0.2 to 0.4N in acid

$$Cr_2O_7^{--} + 6I^- + 14H^+ = 2Cr^{+++} + 3I_2 + 7H_2O$$

Prepare N/10 potassium dichromate solution by dissolving 4.903 gm. of the 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 four 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 gm. of potassium iodide. Allow the reaction to proceed in the dark for five minutes, then dilute to 400 ml. and titrate with the Sodium Thiosulfate solution adding starch toward the last."[6]

$$\text{ml. x normality of sodium thiosulfate} = \text{ml. x normality of potassium dichromate}$$

$$\text{Norm. of Sod. Thiosulfate} = \frac{20 \times 0.1}{19.867}$$

$$= 0.1008$$ (Data taken from table A.1)

(ii) Standardization of Iodine Solution

$$\text{ml. x normality of iodine solution} = \text{ml. x normality of sodium thiosulfate}$$

$$\text{Norm. of Iodine Solution} = \frac{48.033 \times 0.1008}{25}$$

$$= 0.1934$$ (Data taken from table A.2)

5. Sample Calculation

For Run No. 7:

Volume of treated iodine solution = 25 ml.

Volume of sodium thiosulfate solution required = 19.8 ml.

Normality of thiosulfate solution = 0.1008

$$\text{Normality of treated iodine solution} = \frac{19.8 \times 0.1008}{25}$$

$$= 0.0792$$

$$\text{\% iodine removed} = \frac{\text{Normality of Iodine Stock Solution} - \text{Normality of Treated Iodine Solution}}{\text{Normality of Iodine Stock Solution}} \times 100$$

$$= \frac{(0.1934 - 0.0792) \times 100}{0.1934}$$

$$= 59.2$$

B. Molasses Test

1. Reagents

Molasses Solution	40 gm. of molasses together with 30 gm. of disodium phosphate (buffer), is dissolved in 1 liter of water and sufficient phosphoric acid is added to give a pH of 6.5. The mixture is diluted to 2 liters. It is then filtered through a 1/4 inch thick layer of filter placed on a filter cloth in a Buchner funnel.

2. Test Procedure

(i) Pour 50 ml. of molasses solution into a 150 ml. beaker.

(ii) Add 0.5 gm. of coke and stir until wetted.

(iii) Bring the mixture to boil, and filter immediately through a No. 5 Whatman paper in a gravity funnel.

(iv) Measure the % transmittance of light through the filtrate as explained below.

3. Evaluation

A Beckman Model B Spectrophotometer was used for determining the % transmittance of light through the molasses solution. Distilled water was used as the standard and a light wavelength of 450 angstroms was used.

APPENDIX II

DATA

Table A. 1

Data

Standardization of Sodium Thiosulfate Solution

Vol. of Potassium Dichromate Soln., ml.	Norm. of Pot. Dich. Soln.	Vol. of Thiosulfate Required, ml.	Avg. Vol. of Thiosulfate, ml.
20	0.1N	19.9	
20	0.1N	19.9	19.867
20	0.1N	19.8	

Table A. 2

Data

Standardization of Iodine Solution

Vol. of Iodine Soln., ml.	Vol. of Thiosulfate Soln., ml.	Norm. of Thiosulfate Soln.
25	48	0.1008
25	48.1	0.1008
25	48	0.1008

Table A. 3

Data

Iodine Test*

Run No.	Vol. of Sodium Thiosulfate Required, ml.
Original Coke	39.5
Columbia, H-512-101	4.9
Barnaby-Chaney SK-1	16.1
1	22.2
3	22.3
4	24.5
5	34.0
6	29.0
7	19.8
8	28.5
Vickburg No. 18	24.7
Vickburg No. 19	21.0
9	34.8
10	44.0
11	38.8
12	22.9

* Volume of Iodine Solution = 25 ml.

Table A. 4

Data

Molasses Test**

Run No.	% Light Transmittance
Original Coke	42
Columbia H-512-101	69
Barnaby-Chaney SK-1	98
1	76
3	78
4	48
5	52
6	55
7	82
8	65
Vickburg No. 18	74
Vickburg No. 19	84
9	53
10	62
11	56
12	73***

** % Light Transmittance of Molasses Stock Solution Was 51

*** Molasses Solution Was Turbid, Reading May Be Inaccurate

Table A.5

Data

Check on Reproducibility of Iodine and Molasses Tests

Run No.	Vol. of Sod. Thiosul. Reqd.* ml	% Light Transmittance**	% Iodine Removed*	% Light Transmittance***	% Iodine Removed***
Columbia, H-512-101	4.9	68	89.2	69	89.7
Barnaby-Chaney SK-1	16.4	99	64.1	98	66.5
1	24.1	76	47.5	76	50.6
3	23.0	78	49.7	78	50.1

* Normality of sodium thiosulfate solution = 0.1008
Normality of iodine stock solution = 0.1844
Volume of iodine solution = 25 ml

** % light transmittance of molasses stock solution = 51

*** From Table 5.1

NOTE: The maximum deviation in test results is for the iodine test for Run No. 1. The figures for % iodine removed are 50.4 and 47.5. Thus, the iodine adsorption test and the molasses test for the carbons retested were reproducible within ± 6 per cent.