Destructive distillation of Brophy coal by low-temperature carbonization

by Takeshi Utsumi

A THESIS Submitted, to the Graduate Faculty in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering

Montana State University

Abstract:

This thesis presents the respite of the analyses of the byproducts produced by the low-temperature coal carbonisation project.

It also presents the design of a coal tar still for the commercial plant of the project in Red Lodge, Montana.

The first chapter consists of coal, coke, and sulfur analyses with the drying test of Brophy coal from Bed Lodge. Coals from Norway, North Dakota, Colorado, Utah, and three different Coal mines in Bed Lodge, Montana were analysed. Various cokes produced by the batch-, the pilot-, and the commercial plant were analyzed. Sulfur analyses indicated 1.57, 1.31, 3.55 and 3 per cents of sulfur in Brophy Coal, in the coke, in the tar, and in the coal gas, respectively, A drying test of Brophy coal showed that it has two constant drying rates after the falling rate period.

The second chapter deals with the by-products formation from various coals with the correlation of the carbonisation temperature, The results were discussed of the amounts of the by-products produced from coals mentioned above. Special studies of the by-product formation from Brophy coal found that the best carbonization temperature was between 1100°F and 1200°F in. order for the coke to contain less than 5 per cent volatile matter, and for the maximum yield of tar.

The third chapter consists of the coal tar analyses and the design of a distillation still for the commercial plant. The properties of the tar after centrifuging at the plant showed the necessity to reduce the light. Oil content under SlO0C and the heavy oil content over 355°C in order to meet the grade A specification of creosote by American Mood Preservers' Association for coke residue, For the design of the distillation still, attention was paid to the water contained in the tar, and on low fuel consumption. The plant consists of two stills, two condensers, one heat exchanger, and a steam boiler. It separates water from the tar and produces about 39 lbs, per hour of light oil, 442 lbs, per hour (52 gals, per hour) of creosote* and 72 lbs, per hour of pitch. This plant can be operated in any intervals, but the steam boiler can supply steam to the coking plant operation regardless of the operation of the distillation still.

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LOW-TEMPERATURE CARBONIZATION

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A THESIS

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partial fulfillment of the requirements

for the degree of

Master of Science in Chemical Engineering

at

Montana State College

Approved:

Lloyd Berg

Head, Major Department

Lloyd Berg

Chairman, Examining Committee

Leon H Johnson

Dean, Graduate Division

Bozeman, Montana

August, 1957

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ABSTRACT

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The first chapter consists of coal, coke, and sulfur analyses, with the drying test of Brophy coal from Red Lodge. Coals from Norway, North Dakota, Colorado, Utah, and three different coal mines in Red Lodge, Montana were analyzed. Various cokes produced by the batch-, the pilot-, and the commercial plant were analyzed. Sulfur analyses indicated 1.57, 1.31, 3.55, and 3 per cents of sulfur in Brophy coal, in the coke, in the tar, and in the coal gas, respectively. A drying test of Brophy coal showed that it has two constant drying rates after the falling rate period.

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The third chapter consists of the coal tar analyses and the design of a distillation still for the commercial plant. The properties of the tar after centrifuging at the plant showed the necessity to reduce the light oil content under 210°C and the heavy oil content over 355°C in order to meet the grade A specification of creosote by American Wood Preservers' Association for coke residue. For the design of the distillation still, attention was paid to the water contained in the tar, and on low fuel consumption. The plant consists of two stills, two condensers, one heat exchanger, and a steam boiler. It separates water from the tar and produces about 39 lbs. per hour of light oil, 442 lbs. per hour (52 gals. per hour) of creosote, and 72 lbs. per hour of pitch. This plant can be operated in any intervals, but the steam boiler can supply steam to the coking plant operation regardless of the operation of the distillation still.

INTRODUCTION

INTRODUCTION

Montana is called the "Treasure State". This might be true as far as silver and gold in the early days, and for copper, zinc, and manganese at the present time. However, it would be the Treasure State with its vast and varied coal resources, if the grade was high enough to meet the requirements of present industries in the United States, from economical view-point.

The low grade of the coal has been the bottle neck in the promotion and development of coal mining and coal industry in Montana. Another disadvantage, industry has been changing its power source from coal to petroleum, electricity, and may possibly make use of nuclear energy in the future.

The original purpose of the low-temperature carbonization project at the Engineering Experiment Station of Montana State College was to investigate the possibility of establishing a coke industry in Montana. In spite of the disadvantages and natural trend mentioned above, this project has the following advantages in Montana and surrounding areas, such as the readily available markets of various smelting industries, the low transportation cost, and ample supply of raw material.

Having inherited a similar work of carbonization of Montana coal in Melstone, Montana from P.D.P. Processing, Inc., this project was started in 1952. The early works of this project were done, first on the construction of the prime experimenting apparatus by Rudy Herzel (3) and the investigation of various types of coal with the apparatus by Gordon Smith (5). Second, this project was developed with the design of a continuous charring pilot plant by Robert Quesenberry (4) and was operated by John Goodenbour (2). The third stage of this development was done by Allen Ackers (1), who designed a commercial plant of a continuous low-temperature carbonization in Red Lodge, Montana. Since these investigations were mostly subjected to the production of metallurgical grade coke, it would be natural that the fourth stage was to investigate the utilization of its by-product, tar.

Although coal and its derivatives were well-known from ancient times, the composition of coal and the components of the by-products are scarcely known even at the present time. However, regardless of whether the tar is the main product or the by-product of the coal industry, the importance of the tar can be proved by the fact that almost all of the substances in the tar, like naphthalene, can not be produced by any commercial synthetic methods at the present time, or possibly in the future, and that the washing oil at the benzene recovery plant of coal industry can not be made from any source other than coal tar. Therefore, the primary experiments of coal by-products must be carefully investigated in order to know the amount of valuable by-products from coal.

This thesis consists of three parts: first, the analyses of coal, coke, and sulfur; second, the analyses of by-product formations from various coals and the correlations of the by-product formations from Brophy coal with the carbonization temperature; third, the specification and the boiling point experiments of coal tar as the fundamental research of the tar distillation column design.

The apparatus with which this thesis is concerned is included in three different types of coking plants. First is the batch plant, Figures 1 and 2, called a small retort; second, the P.D.P. pilot plant at Montana State College shown in Fig. 3; third, the commercial plant at Red Lodge, Mont. (1), which is now in operation with the modified design of the above pilot plant.

Because the commercial plant is proposed to utilize Brophy coal at Red Lodge, the data in this thesis are mainly concerned with this coal and its by-products.

In this thesis, the term "coke" is used when referring to a coal which agglomerated when carbonized. If no agglomeration or fusing takes place during carbonization, a striated product usually results and this will be called "char".

Chapter I

ANALYSES

Section I

Analyses

I. Introduction

In any process industry the material balance is the fundamental requirement of its operation. This begins from the analyses of feeding material and ends to those of final products.

Although the material balance of the coking pilot plant at Montana State College could not be completed this year due to the unsteady operations caused by the inconvenient coal and coke storage facilities, this section describes the sampling methods of coal and coke, their proximate analyses, and the sulfur analyses of them.

II. Sampling Methods and Preparation

A. Sampling methods

Because of the criticisms made of the author's analyses of North Dakota lignite coal, the author reviewed several references on standard sampling methods (2) (4) (9) (13). However, the author found these methods were too complex to use at the plant, and therefore did not use them. Also, another reason was that the coal at the plant should have enough mixing history during its transportation from the mine.

However, for the coal or coke storage pile, several points were chosen for taking a shovelful sample from each point and the total weight of these samples was approximately 25 lbs.

During the plant operation, the sample of coke was taken at the outlet of water-cooled auger at proper time intervals.

B. Preparation

Although standard equipment is necessary for the preparation of a sample according to the ASTM methods, the following procedures were usually applied and gave satisfactory results.

Fig. 4 shows the largest particle size in a sample with its amount recommended in the reference (2).

1. Coal

a. Jaw crusher: First, 20 to 25 lbs. of the original sample was passed through a jaw crusher three times, reducing the largest size to approximately a half inch.

b. Coffee-mill type of grinder: Less than 300 gr of ground coal was transferred to a small coffee-mill type of grinder reducing the size to finer than 20 mesh. This was immediately stored in an air-tight container lest the moisture should decrease or increase.

c. Small Riffle sampler: Sometimes this sampler was conveniently used, but usually the air-tight container was shaken just before a sample was taken.

2. Coke

Preparations similar to those used for coal were applied for coke samples, for use of the jaw crusher. The ground sample of coke was placed in an air-tight container because coke easily absorbs moisture from outside.

III. Coal Analyses

The principal elements in coal are carbon, oxygen, hydrogen, nitrogen, and a portion of sulfur combined in very complex molecules with high molecular weights by the coalification reactions. Attempts to isolate individual organic compounds in coal have been almost entirely unsuccessful.

Therefore, the primary methods for the analysis of coals are the proximate analysis and the ultimate analysis. The former is most widely employed for industrial use because it is a quick and easy method for an analytical laboratory with average equipment.

The proximate analysis described in a bulletin of the U. S. Bureau of Mines (6) was mainly used here, though slight changes were made according to the variation of apparatus.

A. Proximate analysis

The well-cleaned porcelain crucible (15 c.c.) was used for the container of about a one-gram sample. Weighing was performed by the four decimal balance throughout the analysis. Each sample was run six times.

1. Moisture

There are two kinds of moisture analyses (9): one is for the primary moisture on the surface of the coal, the other is for the secondary moisture in the coal. The first analysis requires a heating period of 24 hours at 50°C. Although the primary moisture analysis was used once with the drying test for the ground coal by a jaw crusher as shown in Figures 5 and 6, usually the moisture in the coal was measured by putting the crucible containing the sample into a constant temperature dryer at 100°C for 2 hours. Fig. 7 shows the minimum required drying period of about 1.5 hours.

The difference between the equilibrium moisture contents in Figures 5 and 7 was caused by the reduction of the particle size, as the reference (2) mentions. The same phenomena occured with the analysis of Brophy coal as shown in Table I.

2. Volatile matter

The Muffle furnace built by Gordon R. Smith (11) was conveniently used for this analysis at 800 ± 25°C for 7 minutes.

3. Fixed carbon

This was determined by the difference of other components.

4. Ash

The same electric furnace as for volatile matter was used with air supply for over-night.

B. Discussion of results

Table I shows the data for coals from Norway, North Dakota, Colorado, Utah, and from three different coal companies in Red Lodge, Montana. Special analyses were made for 42 different carload samples at the request of Brophy Coal Company in Red Lodge, Montana.

Concerning the commercial carbonization plant designed for use of Brophy regular coal, the average analysis of its coal is 7.62 per cent moisture, 33.85 per cent volatile matter, 50.35 per cent fixed carbon, and 8.18 per cent ash. Though the values for Brophy fine coal are different from these values of regular coal, the consistencies are shown on dry basis in Table II. Therefore, special attention has to be paid to the drying of the fine coal before its use in operation, thus lessening the difficulty in separating water from tar.

The criticism of an analysis of North Dakota lignite coal mentioned in Section I-II-A must depend on the different sample, and not on the sampling methods in the author's laboratory, because not only the values on wet basis in Table I are so different from each other, but also the values on dry basis in Table II are very different.

The analysis results on Montana Iron & Coal Co. are poor in volatile matter and ash contents compared with Brophy coal, even though the two companies are in the same location.

The results of Colorado coal and Utah coal show higher volatile matter content and less ash content than those of Red Lodge, Montana coals.

C. Screen analysis of Brophy coal

Table III shows the screen analysis of Brophy fine coal. About 57 per cent is larger than 3/16", 74 per cent is larger than 3/32", and 83 per cent is larger than 3/64".

IV. Coke Analysis

The same methods as for coal were applied for coke analyses according to the bulletin of the U. S. Bureau of Mines (6), although the moisture was measured only for samples from the storage pile. Later, the moisture analyses were required for the samples from the P.D.P. pilot plant operation, because the coke in the auger was sprayed with water before sampling.

In this paper, three coke analyses are listed, two of them in Table IV, one on Figures 8 to 15. The first are the analyses of coke produced by a small retort, the second of coke from the storage pile produced by the P.D.P. pilot plant. The third are the analyses of the volatile matter in the coke during P.D.P. pilot plant operation. This volatile matter variation is compared with the other variables of the plant operation.

A. Analyses of coke produced by the small retort

The results of these analyses will be discussed with the production of tar in the next chapter.

B. Analyses of coke produced by the P.D.P. pilot plant

The analyses of this coke were sampled from the storage pile, so that the data in Table IV include the moisture analyses. Also, these were converted to dry basis for the comparison with other analyses.

On dry basis, the analyses of coke produced from Brophy regular coal show the fact that the volatile matter in fine coke is less than in coarse coke, and the fixed carbon of fine coke is larger than that of coarse coke. This might be caused in the carbonization period, because fine coal particles would be easily carbonized and volatize its components. The analyses of the coke produced from Brophy fine coal also shows about the same results as for the fine coke from Brophy regular coal. Therefore, a briquet process of fine coke may be possible in the future, if the economic situation permits. Usually the fine coke involves less moisture than the coarse coke. This is caused by the difficulty of moisture vaporization in porous larger coke.

C. Volatile matter analyses of coke from the pilot plant operation

Figures 8 to 15 are the graphic expressions of volatile matter percentages versus time, compared with the heat blower temperature, carbonization temperature, the feed gas rate, and the auger speed.

The purpose of these graphs is, first, to find the correlations among the variables; second, to find the most effective variable on the volatile matter change; third, to set the limitations of the variables. Although it is very hard to predict from these short periods of plant operation, and from the few data on the auger speed and volatile matter, the writer summarizes the results and recommendations from the investigations of the figures as below:

1. Correlations

The volatile matter first depends on the carbonization temperature, and the temperature depends on the feed gas rate and the auger speed. The temperature and other two factors are restricted with the upper limit of the heat blower temperature not to exceed 1200°F.

The change of the feed gas rate seems to appear more rapidly on the heat blower temperature rather than on the carbonization temperature. Conversely, the latter is more easily affected by the auger speed.

Therefore, though the volatile matter, of course, depends on the carbonization temperature, it also largerly depends on the auger speed. Namely, a slight change of the auger speed seems to have considerable effect on the volatile matter.

It is the author's opinion that the speed of the auger is not a negligible factor and should be recorded in the data.

The change of the carbonization temperature seems to appear on the volatile matter about 30 to 60 minutes later. This means that the travel of the coke takes that much time from the middle of the retort, where the thermocouple of carbonization temperature measurement is located, to the outlet of the auger.

Therefore, though the previous researcher mentions about 15 to 20 minutes for the required carbonization period (1), the author expects about 60 to 90 minutes for the entire period of carbonization from the top of the retort to the outlet of the auger. This typical example is shown on Fig. 9 at the change of feeding coal from Brophy regular coal to Routt coal.

Although the change of the feed gas rate appears on the temperature of the heat blower in a half hour or so, the change in the carbonization temperature does not appear for another 30 minutes.

Therefore, combining with the required time period from the carbonization temperature to the volatile matter, 30 to 60 minutes, the total time lag between the changes of feed gas rate and of the volatile matter probably ranges from 90 to 120 minutes.

However, because the change of the auger speed appears on the carbonization temperature in 30 minutes, the total time lag between the auger speed and the volatile matter changes in probably 60 to 90 minutes.

The volatile matter change of Run No. 10 is fairly smooth, but the total average is higher than those of other runs, even though the carbonization temperature is about 50 to 100°F higher than others.

This might be caused by seasonable weather, that is, most of the heat supplied was consumed for preheating and drying of coal wet by snow. Although there is no data on the auger speed, if the same speed was applied as before, the carbonization period was not long enough for wet coal in winter. Probably in cold weather, the carbonization zone could go down close to the bottom of the retort.

The seasonable change also affected the gas feed rate. Comparing Fig. 8 with Fig. 15, the gas feed rate of the latter is about double the former, to get about the same volatile matter percentage. Namely, the same percentage of volatile matter in summer can be obtained with less gas feed rate and lower carbonization temperature than in winter.

2. Variables

As mentioned above, the most effective variable on the volatile matter is the carbonization temperature, but the temperature is affected more by the auger speed than by the feed gas rate change.

Although the main purpose of the plant operation is to obtain a coke with volatile matter less than the 5 per cent specification, it takes quite a bit of time for information regarding the percentage of volatile matter to reach the operator; for instance, 1.5 to 2 hours from the change of the feed gas rate to the sampling, and 1.0 to 1.5 hours from the change of the auger speed to the sampling. Also, the analysis of the volatile matter takes at least one hour, and may be delayed to the next day.

Therefore, the plant operator has to guess from the carbonization temperature what percentage of coke will come out from the auger in the next 30 to 60 minutes.

Since the carbonization temperature change is delayed about 30 to 60 minutes from the feed gas rate change and 30 minutes from the auger speed change, the operator has to judge what will happen on the carbonization temperature by the change of the feed gas rate or the auger speed after the above time period. Also, he must be able to judge what will happen to the volatile matter after 1.5 to 2.0 hours after the change of the feed gas rate, and 1.0 to 1.5 hours after the change of the auger speed.

The author considers the carbonization temperature a main control indicator; the heat blower temperature, a minor control indicator. The feed gas rate and the auger speed are the main control factors of the retort operation, the latter showing its change more quickly on the carbonization temperature than the former.

The author would like, if he could assemble enough data on the steady operation, to investigate how much change of feed gas rate or auger speed makes how much temperature change on the carbonization temperature, and the same for the change of volatile matter.

3. Limitations

The temperature of the heat blower and carbonization in the retort are the two control indicators. The former was maintained close to 1200°F and the latter between 1000°F and 1200°F, usually keeping the difference between them from 100 to 200°F. Although the carbonization temperature increases with the increase of the heat blower temperature, the carbonization temperature was preferably kept under 1050°F, because the heat blower becomes red hot over 1200°F.

However, considering the results of the coke analyses from small retort experiments, the author's opinion is that 1050°F is the border line to obtain the coke under the 5 per cent specification. That is, the results would be much better if the retort could be operated between 1050 and 1200°F, probably the best between 1100 and 1200°F.

4. Miscellaneous

Concerning the results of the coke analyses from small retort experiments, the author thinks that most carbonization takes place under the middle of the retort where the thermocouple measuring the carbonization temperature is located. Then, the retort will be divided into the following zones from the top of the retort: first, the preheating zone; second, the drying zone evolving mostly water; third, the primary carbonization zone evolving mostly the light part of the volatile matter; fourth, the carbonization zone evolving the middle and heavy parts; and fifth, the final carbonization zone evolving mostly pitch and tar.

Because the author thinks that the final zone is important for producing the volatile matter under the 5 per cent specification, he desired to set another thermocouple in the zone close to the outlet of coke.

Figures 8 to 15 would be convenient for the plant operation and should be drawn during the operation. From these figures it may be possible to develop a quality control chart setting the proper limitations of the variables.

This year, due to the interruptions caused by construction on the campus, the total plant operation period for taking data was unfortunately very short, 386.5 hours, or about 16 days throughout the year. Therefore, it is hard to predict the exact factors from these data and it will be necessary to analyze the factors in the figures from future data.

D. Analyses of coke produced by the Red Lodge commercial plant

The results of the coke produced at the commercial plant in Red Lodge, Montana are shown in Table IV.

The values of the volatile matter on dry basis are fairly improved compared with the results of the coke produced at the pilot plant of Montana State College. The main reason is probably the use of a higher carbonization temperature at the Red Lodge commercial plant than at the pilot plant. The lower volatile matter content also results in the higher fixed carbon content than those of the cokes produced at the pilot plant.

As mentioned before, the volatile matter of coarse coke is higher than that of the fine coke; therefore, there is less fixed carbon in coarse coke than in fine coke.

V. Sulfur Analyses

A. Introduction

In the chemical industry, sulfur may be of the sources of corrosion. Once during the author's experiments, the steam heating copper pipe in the tar distillation column was badly corroded and made it necessary to investigate the sulfur content in the tar.

Also, the material balance of the P.D.P. pilot plant was being investigated at the same time, the researcher analyzed the sulfur in Brophy regular coal and coke, trying to establish the material balance of sulfur throughout the plant.

B. Analyses

Sulfur in coal usually occurs in the form of inorganic and organic compounds, and mostly as FeS_2. The analysis of sulfur in coals is classified into three kinds: total sulfur, incombustible sulfur, combustible sulfur, depending upon the sulfur state in coal, and pyrite, sulfate, or organic sulfur, respectively (9).

In this section only the total sulfur in coal was analyzed following the ASTM standard method (4).

C. Data

Table V shows the results of sulfur analyses: 1.57 per cent in Brophy regular coal, 1.31 per cent in Brophy regular coke, and 3.55 per cent in the tar residue produced from Brophy coal.

Comparing this with the values noted in the literature, reference (13) quotes 0.5 to 3.0 per cent for American coals now utilized in industry, although it may run to 5 per cent in some western coals.

Reference (3) shows about 1 per cent for Montana coal and 3.54 per cent for North Dakota lignite. Reference (8) shows 0.33 per cent for Wyoming coal, 1.42 per cent for North Dakota coal.

D. Material balance

Fig. 16 shows the material balance of the plant and the sulfur. The data of the former were obtained from the results of by-products analyses by small retort experiments. The weight percentages of the by-products shown in the figure are represented by the rectangular area.

The calculations of sulfur percentages based on the total sulfur in the original coal show the fairly matched results with the values of the reference (13). On the other hand, the material balance of the by-products at P.D.P. pilot plant would be within the limits shown in Fig. 16.

VI. Drying Test of Coal

In the coal carbonization industry, the water content in coal causes more heat consumption in the retort and the difficult separation of it from the tar in the by-product recovery process, so that a preheating and drying process before carbonization might be valuable. Also, for the P.D.P. carbonization process, a gas with a heating value as high as 950 B.t.u. per cubic foot of coal gas (13) is produced at about 4000 to 5000 ft^3/ton of coal as described in the next chapter. Therefore, the author intended to utilize this waste gas for the drying of coal, but he could not complete the design for the continuous rotary dryer.

The primary experimental results are shown in Figures 5 and 6. Concerning the drying rate of coal shown in Fig. 6, the constant drying period is not shown but the falling rate period is. Usually, according to the drying theory (5), there should not be any constant drying period after the falling rate drying period. However, the reference (7) shows a constant period after the falling rate period for the drying experiment of rice, and the reference (12) shows the upward curve after the falling rate period for the drying of paste. As mentioned in the latter reference, these phenomena are caused by cracking of the drying material and exposing the new wetted surface to the drying air. Therefore, these constant rate drying periods of coal in the author's experiment were probably caused by the same reasons as those given in the references.

The part of the straight line in Fig. 6 is expressed as,

$$\frac{dx}{dt} = 2.12x - 0.12 \qquad (1)$$

where

$\frac{dx}{dt}$ = drying rate (lbs. H_2O/hr. lbs. of dry coal)

x = free moisture content (lbs. H_2O/lbs. of dry coal)

Chapter II

BY-PRODUCTS FORMATION

BY

LOW-TEMPERATURE CARBONIZATION

Section I

By-products Formation from Various Coals

I. Introduction

The formation of substances in coal by-products is usually thought of as the thermal decomposition of the volatile matters in coal. The mechanism of the reaction is difficult to determine, because of the high temperature of the decomposition, the barely known chemical structure of coal, and of the complex conditions in the coke-oven. Therefore, only a few of the quantitative relationships have been investigated to date, especially for high-temperature carbonization.

This chapter is primarily concerned with the analysis of the by-products of low-temperature carbonization. It further includes the gathering of the general concepts concerning the amount of the by-products and their relationships to the carbonization temperature.

This section will be devoted to the analysis of the by-products from various coals.

II. Experimental Procedures

About 250 gr. of clean quarter-inch alundum balls were placed on the bottom of the small retort and the ground coal was put above this filler. The filler and ground coal were separately weighed and recorded before conducting the experiments.

Three Variacs were set at the same wattages with a watt meter. After all of the apparatus were set as illustrated in Fig. 2, the following readings were taken at 15 minute intervals; the temperature in the retort, the temperatures of the container, and the volume of the gas released.

When the gas was being released at a rate of less than 0.002 ft^3 per minute, the heaters were turned off, and the total amount of by-products in each container was weighed. The filler and coke were also weighed together, and the loss in weight was assumed to be the by-products released. Since the first container contained a large volume of water, the products were placed in the centrifugal separator which enabled the measuring of the amounts of light oil, water, and heavy tar.

III. Apparatus

The old small retort, which was used for over a year, was completely altered due to numerous complications. One example was the plugging in the first condenser by heavy tar which caused errors in by-products calculation. Another difficulty was that controlling the power input to the retort by an ammeter caused inconsistent temperature distribution in the retort throughout the experiment.

The packed column of the old apparatus was further replaced with condensers, since most of the tar mists remained on the surface of the packings instead of condensing in the containers.

Fig. 1 and 2 show the old and new apparatus for the small retort experiments.

The method of temperature control in the retort was changed from ampere to wattage, since the ampere method failed to give a linear function with the temperature.

The heavy tar was deposited in the first condenser of the old apparatus, even though the water level in the cooling tank remained lower than the condensing tube. Therefore, the condenser was changed to a vertical situation immediately following the outlet of the retort to let heavy tar flow down easily. Also, the new condenser was made of glass, which enabled the operator to prevent the plugging of heavy tar in the center tube and to change the coolant to warm water. Temperatures in the containers were measured.

The condensers at the outlet of the containers were to ensure the condensation of as much light oil as possible. Furthermore, they were set vertical, for it was often necessary to force the condensate down by warming the outside of the center tubes. The last condenser being larger than the others, was used to condense all of the light oil. This was not placed vertical because of its original form.

IV. Results of Experiments

The results, as indicated in Table VI, show the amount of by-products produced from various coals at low-temperature carbonization. The data on the amount of oil and water produced from Knife River lignite and Routt coal are not listed on the table since the old small retort was used throughout the experiments.

A. Coke

1. Coke yield

Although these data can not be compared with each other due to the different carbonization temperatures, generally speaking, Norway coal had the best yield of coke, about 80 per cent on wet basis. On the other hand, North Dakota lignite coal had the poorest yield, about 50 per cent. The yields from three coals are 69 per cent for Colorado coal, 64 per cent for Utah coal, and 63 per cent for Red Lodge, Montana coal.

2. Coke analysis

On coke analysis, Norway coal had the smallest ash content of about 9 per cent and the highest fixed carbon content of about 88 per cent. The lignite coal from North Dakota produced the reverse results; that is, the largest ash content of about 18 per cent and the smallest fixed carbon content of about 71 per cent. The values from the other three coals ranged from 10 to 17 per cent of ash and from 74 to 86 per cent of fixed carbon. For volatile matter, Norway coke produced a fairly small volatile matter content as compared to the highest value from Colorado coal.

B. Oil

1. Oil yield

Norway coal had a smaller oil yield than American coal. This indicates that the Norway coal is best suited for coking coal but not for the coal tar industry.

Utah coal produced more oil than Red Lodge coal. One explanation may be the higher volatile matter content found in Utah coal than in Red Lodge coal.

2. Specific gravity

The determination on the specific gravity of oil was an approximation because of the difficulty involved in separating water from oil and of the small quantity of oil produced. The data on Table VI show that Norway coal produced more light oil than American coals. The specific gravity of oil from Red Lodge, Montana coal was close to the specification value of creosote.

C. Aqueous distillate

In the tar industry, the separation of water from tar or light oil is always a problem. Although Norway coal showed the lowest water content, this was probably due to the coal being ground and dried before shipment. Red Lodge coal produced twice as much water volume as oil. Besides the high water content being a probable characteristic of Red Lodge coal, the fact that the coal was received coarse and wet may have been the reason. Therefore, the separation of water from Red Lodge coal would be a problem in its by-products recovery process.

D. Gas

1. Gas amount

The volume of gas produced from American coals fell between 4000 to 6000 ft^3 per ton of coal. In contrast, Norway coal produced a gas volume between 1500 to 2300 ft^3 per ton of coal. The data of Shreve (11) showed about 3000 to 4000 ft^3 of gas produced per ton of coal for the low-temperature carbonization of American coals, indicating that the results obtained are probably correct.

2. Approximate density of coal gas

The weight losses were considered to be due to the escaping gas. These losses were converted into the density of coal gas and the results coincided with the values given in the text of Babcock and Wilcox (3).

Section II

By-products Formation from Brophy Coal

I. Introduction

This section concerns the finding of the mechanism of coal carbonization at low-temperature, and a comparison of the results with the previous data as cited in various literature. Furthermore, since the commercial plant of P.D.P. Processing, Inc. at Red Lodge, Montana is utilizing Brophy coal, these experiments were especially devoted to the investigation of the relationships of Brophy coal carbonization with the carbonization temperature.

The experimental procedures and apparatus used in this section were similar to those of Section I.

II. Summary of Results and Discussion

The results of by-products formation from Brophy coal at low-temperature carbonization were tabulated in Table VII and graphically expressed in Figs. 17 to 23.

A. Coke

1. Coke yield

As shown in Fig. 17, though there are not so many data at high temperature, the curves of weight percentage yield of Brophy coke are fairly similar to those of the references. And, as converting to dry basis, the curve of Brophy coke very closely fits them.

Although the yield of coke, weight percent, at high temperature carbonization beyond 700°C becomes constant, the percentages around 500 or 600°C varies widely. For the P.D.P. plant operation, the retort temperature between 1000 to 1100°F correspond to this region. Therefore, the temperature control in this region must be very important in affecting the amount of coke yield, the other by-products yield, and the percentage of volatile matter. This is because the coke under 5 per cent of specification value will be obtained over 600°C as shown in Fig. 18, and because the oil yield shows the maximum yield around 600°C.

As for the upward part at low temperature, the writer recalls the difficult operation of Routt coal from Colorado which included high volatile matter. As the temperature decreased under 1000°F, the volatile matter in the coke increased so rapidly that the operators could not find the right temperatures for the desirable volatile matter content, 18 per cent. This condition also shows up in the curve of coke percentage, Fig. 17.

2. Coke analysis

a. Volatile matter

Fig. 18 shows the volatile matter content in coke versus carbonization temperature. The points are scattered over a wide range because the volatile matter analysis depends greatly on the temperature and the time period in a furnace during the analyses. However, it would be noticed that the temperature around 500 to 600°C are the lowest temperature necessary to obtain under 5 per cent volatile matter in coke.

b. Fixed carbon

Fig. 19 shows the fixed carbon content in coke versus carbonization temperature. The results of Brophy coal are about 10 per cent lower than that of the reference, which presumably was caused by the higher ash content. Although the curve becomes level at high temperature, 75 per cent of specification value can be obtained satisfactorily at any temperature over 500°C.

c. Ash

Fig. 20 shows the ash content in coke versus carbonization temperature. The curve of Brophy coke is fairly flat and is about one per cent higher than those of the references. It will be noticed that the curves decrease with decrease in temperature. The total amount of ash in unit coke should be the same. This fact would be caused by the correlation with volatile matter percentage which increases rapidly with temperature decrease.

A comparison of the values in Fig. 18, 19, and 20 with the data of the P.D.P. pilot plant operation in Table IV shows that the latter on dry basis correspond to the results of the small retort at about 500°C (930°F).

B. Oil

1. Oil yield

The results in Table VI show that more light oil than tar was produced from a ton of coal. This fact is the reverse of the results in the reference (6). However, during the experiments the author noticed that the oil by-product was hard to separate from the water and it was hard to determine the density because this oil always changed its density with an unknown factor. Also, if the term "tar and light oil" were determined according to the boiling point range, the samples of oil were too small to make the boiling point test. Therefore, Table VII shows a comparison of the total yield of oil with the summation of tar and light oil in the reference (6).

Table VII shows the maximum tar yield to be around 600°C for about 19 gals. of oil from one ton of Brophy coal. This value is smaller than that of the previous researcher (1), but it might be caused by the conversion factor using different densities.

Again, the author would say that the carbonization temperature around 600°C is also the important point for oil yield.

2. Density of tar

The density of tar shown in Table VII is an estimation because of the difficulty of the tar determination as mentioned above.

Assuming the densities of the references (13) and (7) for Brophy tar to be correct, the carbonization temperature around 600°C would produce a tar which meets with the standard specification of density, 1.03, for creosote.

The author's experiences at the settling of tar in a decanter were that some of it stayed at the top, some at the middle of water, and the rest on the bottom. Also, frequently a portion of the top or bottom replaced each other. This means that an indirect water cooler is necessary instead of the present tar trap at the P.D.P. pilot plant, and preferably, a drying process for the coal should precede the carbonization process.

C. Aqueous distillate

Fig. 21 shows the weight percent of aqueous distillate from one ton of coal. The results are about 10 per cent higher than those of the reference which also affected the results of the coke yield as shown in Fig. 17.

This high percentage of water also requires a pretreatment of the coal before carbonization because of the difficulty of separation of the tar in an emulsion state from water.

This also emphasizes the fact that the use of a water cooler at the tar trap is not convenient because the by-products already include a great deal of water and the separation of tar from water is a well-known problem in the coking industry. The reference (12) shows a convenient indirect primary cooler which the P.D.P. commercial plant may be able to apply.

D. Gas

1. Gas amount

Fig. 22 shows the amount of gas produced with a correlation of the carbonization temperature. The results are fairly well matched with the curve of the reference.

The increase in production of gas as the temperature increases is caused by the decomposition of volatile matter in coal and coal gas. This also might be proved from the results in Table VII and Fig. 22. Namely, the higher temperature causes a more rapid decomposition of the coal and lessens the yield of tar, and it also causes the decomposition of coal gas and lessens its density as shown in references (2) and (3).

According to these results, the author questions the data obtained by the previous researcher (1), who obtained around 7000 to 8000 ft^3 of gas from a ton of coal. Presumably, his experiments used higher carbonization temperature, around 800 to 900°C, though he did not indicate the temperature.

2. Approximate density of coal gas

Fig. 23 shows the approximate density of coal gas with the carbonization temperature. This density was calculated by dividing the total weight loss by the gas volume.

In spite of many factors of estimation such as the balance error, the deposition of light oil in the condenser which was not taken into account, and the gas leaking, the results are fairly close to that of the reference.

Although the author could not perform gas analysis, the lighter density of coal gas may be indicated by the high content of the lighter gas compared to that of air as shown in the references (2), (3), and (9).

III. Mechanism of Low-Temperature Carbonization

Because of the complexity of coal substances and carbonization conditions, usually the mechanism of the coal carbonization is not paid attention to; only the final products are considered.

This part of this section is devoted to the analysis of the mechanism of Brophy coal carbonization. As the amount of produced gas was the only measurement of time function, the following discussion is limited to the mechanism of gas evolution at low-temperature carbonization.

The results of Run No. 2 and Run No. 7 were neglected in this section because of their discontinuous heating period.

A. Cumulative gas amount versus time

Fig. 24 shows the cumulative gas amount versus carbonization time. This figure shows the similar curves on an arithmetic graph. Although the carbonization temperature of Run No. 3 is named as 585°C (the final reading), this temperature seems lower than that of other experiments. If the temperature is assumed to be 675°C, there seems some correlation between gas amount, carbonization temperature, and carbonization time.

B. Gas rate versus time

Fig. 25 shows the rate of gas produced versus time. The curves are similar to each other and their characteristics agree with the results of wood carbonization in the reference (10).

For all of these curves it appears to the author that there are three stages on the carbonization mechanism. The first stage is the time lag required for the preheating of the retort, the condensation of water and light oil. The second stage is the steep increase of the gas rate presumably caused by the primary decomposition of coal. The third stage would be the decreasing curve of the rate still evolving the gas decomposed by the secondary reaction.

C. Gas rate versus carbonization temperature

Fig. 26 shows the progress of gas evolution with temperature. The distinguishing point in this figure is that all of the maximum values are gathered between 400 to 500°C, and that they are similar in having a slowly rising curve at the front followed by a steep part up to the maximum point. Then, they fall to their final carbonization temperature. According to the experimental observations, the author presumes that the space on the slowly rising curve was occupied with the water which condensed in containers following its exit from the retort. Also, most of the light oil was probably evolved between 150 and 300°C and condensed in the containers. Therefore, the author can say that the primary decomposition of coal probably occurs under 450°C.

If there had been some devices to measure the original gas amount and the amount of light oil and tar, their amounts would fill up much of the space above the left side of the curves, and would make symetrical curves throughout the carbonization temperature. And also, it would be possible to draw curves for water, light oil, tar, and uncondensible gas which might help to find the maximum points of light oil and tar yields.

D. Carbonization temperature versus time

Fig. 27 shows the carbonization temperature increase with the time. The curves show a similar increase for the cumulative gas amount, but they are not in order with the carbonization temperature.

Chapter III

PRODUCTION OF CREOSOTE

Section I

Properties of Creosote

I. Introduction

Besides coke as the major product of P.D.P. Processing, Inc., coal tar is a by-product.

Coal tar is a mixture of many chemical compounds, such as light oil, pyridine bases, phenols, naphthalene, anthracene, heavy oils, pitch, and other complex compounds. Although the characteristics of coal tar depend on the type of coal, the temperature of carbonization, it is the most inexpensive raw material for supplying benzene, toluene, xylene, and numerous other compounds to the chemical industry.

However, the following descriptions and experiments are focused on the production of creosote from the coal tar at low-temperature carbonization.

The coal tar from low-temperature carbonization is distinguished by its low specific gravity and consists of aliphatic compounds instead of aromatic compounds, which are present in coal tar produced by high temperature carbonization. Fig. 28 shows the variations of coal tar compositions with carbonization temperature. High carbonization temperature causes cracking action on the volatile matter evolved from coal. As the carbonization temperature increases, the loss of the valuable light constituents are vaporized or cracked to gases. Fig. 22 illustrates the effect of carbonization temperature on the amount of gas evolved.

Another limitation is in the specification of creosote. Creosote from wood tar was first used as an antiseptic in England, but with the development of the wood-preserving, the coal-tar industries, and the petroleum industry in recent years, the term creosote gradually came to be applied to the heavy distillates from coal-tar, and the use of the term has become more and more extended. Presently, it is commonly used in referring to the distillates heavier than water from any tar or tar-like substances. Creosote, therefore, is usually named by specifying its source, such as coal-tar creosote, petroleum-tar creosote, water-gas creosote, wood-tar creosote.

Creosote has extensive uses in many fields such as wood preservation, fuel oil, Diesel engine fuel, sheep dips and disinfectant fluids, lubricating grease, black varnish, and roofing paints. For these particular applications the consumers prefer their own specifications according to its use. Even for wood preservation, a number of specifications for analyzing creosote oil have been proposed and are in force. For instance, specifications are published by American Wood Preservers' Association, the American Society for Testing Materials, the American Railway Engineering Association, and by the U. S. Government.

As mentioned above, this paper will be focused on the creosote for wood preservation according to the specifications by the American Wood Preservers' Association, because it is the main purpose of the utilization of coal tar produced by P.D.P. Processing, Inc.

II. Specifications of Creosote-Coal-Tar Solution

Wood preservation is a means of protecting timber from decay caused by fungi, thereby maintaining the original strength of the wood for a long period of time. Coal-tar creosote, because of its long, successful service, has been the leading wood preservative for general use all over the world. It has been shown (11) that 70% of the timbers treated by 4 to 6 lbs. of creosote per cubic foot of wood have retained their original strength for four years, contrasted with untreated timbers after three years.

As the specifications of the American Wood Preservers' Association mentions, standard creosote is a distillate of coal tar produced by high temperature carbonization of bituminous coal. The characteristics of the standard creosote are specified by the specification P 1-52 of the American Wood Preservers' Association. However, coal-tar itself, the mixtures of creosote and coal-tar have also been used for the same purposes of wood preservation. The reason for using coal-tar and the mixtures is to reduce the price of the wood preservatives. The characteristics of the mixtures are specified by the Association's specification P 2-51. Therefore, considering the coal-tar from P.D.P. Processing, Inc. as a mixture of creosote and coal-tar, it is better to compare it with the specification P 2-51 listed in Table VIII.

Owing to the fact that coal-tar creosote is a comparatively cheap article, and that it is an unattractive substance to the research chemist, its composition has not been thoroughly investigated. The author's original assignment was to design a distillation column to separate creosote from coal-tar. Therefore, the experiments on coal-tar were focused on the investigation of the amount of each fraction in the coal-tar.

A. Specification of coal-tar from the P.D.P. pilot plant

Table IX shows the several results of coal-tar produced at the P.D.P. pilot plant of Montana State College and at the P.D.P. commercial plant in Red Lodge, Montana.

1. Light oil from distillation column

Light oil was distilled by a steam heated batch still which separated water from coal tar. Therefore, it is natural that the water content was very small, the specific gravity was lighter than water, and large quantities of light constituents were present. However, as seen in the distillation analysis, some of high boiling fraction were in the light oil, presumably caused by the local super-heating of coal tar on the steam pipe. Though the fixed carbon percentage in the distillation residue was very high, the total percentage in the light oil was very small because of the small amount of the distillation residue.

2. Tar from gas absorption column

The amount of tar from the gas absorption column is given in the second column of Table IX. This tar was allowed to separate from water in a laboratory decanter in a constant temperature bath for 24 hours. Therefore, the water content of these results is fairly close to the specification of creosote-coal-tar solution. The specific gravity of the tar also meets the grade A region of the specification of the American Wood Preservers' Association.

Though the low-temperature coal tar has to show a large quantity of light fraction, the results show very few light oil constituents, but does show a large quantity of distillation residue, which gives a high coke residue percentage. Since the retort had holes on the center cylinder, the light constituents may have been combusted during the carbonization. This trouble influenced high ash content in the distillation residue which was carried over with coal gas. The conclusion on the tar is that it does not meet with the specification of creosote-coal-tar solution in Table VIII.

Assuming the boiling point ranges of the substances illustrated in Fig. 28 as 235°C for light oil and crude naphtha, 315°C for creosote, 355°C for anthracene, the cumulative percentages of these substances gives a decreasing curve with an increase of carbonization temperature as shown in Fig. 29. Comparing these cumulative curves with the results of P.D.P. tar, it is seen that the boiling point range of the tar corresponds to the values around 750 to 775°C in Fig. 29. Therefore, the above mentioned trouble in the P.D.P. retort caused the same cracking action on volatile matter as high-temperature carbonization, even though the operating carbonization temperature was below 600°C.

3. Tar after centrifuging

As mentioned in Chapters I and II, the separation of tar from water is a difficult problem in the coal industry. The problem is that tar occurs as an emulsion in water. Because of the high moisture content in Brophy coal, and because of the direct cooling method of coal gas in the tar trap, the decantation of tar has not been successful in separating the tar from the water. Also, the specific gravity of P.D.P. tar is almost equal to the specific gravity of water. The values are illustrated in Fig. 30.

It was proposed to separate the water from the tar by centrifuging. The sample after centrifuging was analyzed and the results are given in Table IX, which shows the water percentage of 8.10 per cent. This means that the tar has to be distilled in order to meet with the specifications, after it has been centrifuged. Though this water percentage is higher than that of the original crude tar, the two should not be compared because the sample of the crude tar was prepared in a constant temperature bath which can not be duplicated in a commercial plant.

The centrifuge has a mechanism for reducing the coke residue percentage from 16.4 to 11.3 and also reducing the specific gravity from 1.085 to 1.069. This compares favorably to the grade D of the specification for the coke residue and the grade A for the specific gravity specification. For the distillation analysis, the tar after being centrifuged meets with the grade B of the specifications. The percentage of high fraction over 355°C is reduced by centrifuging. The analysis of distillation residue shows about the same results as that for tar from the gas absorption column. This means that the reduction of percent coke residue (free carbon) from 16.4 to 11.3 was caused only by the reduction of the percentage of distillation residue. Namely, it was reduced from 100 − 36.85 = 63.15% to 100 − 57.86 = 42.14%.

4. Crude tar from Red Lodge commerical plant

The commercial plant of P.D.P. Processing, Inc. started its operation in July 1957, and the following descriptions are concerning the results of the first crude tar produced at the plant.

a. Crude tar (Sample No. 1)

The results of the crude tar are shown in Table IX. The specific gravity of this tar is higher than that of tar produced from a pilot plant at Montana State College as shown in the second and third columns of the same table. The reason for this higher specific gravity is probably caused by the higher carbonization temperature used at the commercial plant (1100 to 1300°F) than at the pilot plant. As shown in the references (13) and (7), the specific gravity of tar is increased with the increase of the carbonization temperature. However, this specific gravity of the tar produced at the commercial plant meets the grade A of the specification of creosote by the American Wood Preservers' Association.

The water content in this crude tar is extremely low compared with the water in the tar produced at the pilot plant. This is mainly explained by the fact that the commercial plant does not use the tar trap with water spray, and that the gas absorber in the commercial plant is operated by re-circulated by-products instead of water which was applied at the pilot plant. Another reason is probably the higher specific gravity as mentioned above. Namely, the high specific gravity makes easier decantation of tar from water. This low water percentage meets the grade A of the specification of creosote listed in Table VIII.

However, this does not mean that the crude tar can be sold as commercial creosote without pretreatment, because the results were obtained from the tar which was separated from water by a laboratory decanter left to stand overnight, and because the author observed a large quantity of water on the top layer in the decanter.

About the distillation analysis, large quantities of light constituents were present compared with the results of the crude tar produced at the pilot plant of Montana State College. This fact shows that the commercial plant at Red Lodge completely eliminated the difficulty of the combustion of light oil constituents which troubled us at the pilot plant. This also decreases the amount of the distillation residue from 100 - 36.85% = 63.15% to 100 - 50.20% = 49.80%. However, these results can meet only the grade D of the specification, except for the percentage of the light oil. Another disadvantage of this crude tar is the high distillation residue over 355°C.

Since there is no combustion of light constituents at the commercial plant, the free carbon in the distillation residue is increased from 28.6 per cent for the tar produced at the pilot plant to 37.3 per cent. Namely, the free carbon remained in the tar without evolving as carbon monoxide or carbon dioxide.

This high free carbon content and the high distillation residue causes the high coke residue percentage of 18.3 which does not meet the 11.0 per cent of the grade

D specification as shown in Table VIII.

As it is shown in the results of the distillation analysis, there is no ash in the tar. This means that the coal gas does not carry any dust from the retort to the by-products recovery process.

b. Crude tar (Sample No. 2)

The results of the crude tar (Sample No. 2), which was sampled later than Sample No. 1, are improved to meet the specification of creosote. The results are shown in Table IX.

The water percentage and coke residue percentage are reduced from 2.8 of Sample No. 1 to 2.07 of Sample No. 2, and from 18.3 of Sample No. 1 to 15.5 of Sample No. 2, respectively. Also, the results of the distillation analyses are considerably improved and meet the grade B of the specification, except for the percentage of light oil. The results of the distillation residue are about the same as those of Sample No. 1.

c. Tar after centrifuging

The centrifuge used for the sample of tar produced at the pilot plant was installed at the commercial plant in Red Lodge, Montana.

The results of the analysis of the tar treated by this centrifuge are given in Table IX.

Though the purpose of this centrifuge was to separate water from tar, the water content in this tar was not reduced as the author expected. However, since the author observed a large quantity of water in Sample No. 1 and Sample No. 2, but no water in the tar after centrifuging, the water content in the original sample should show the larger percentages in Samples No. 1 and No. 2, and less percentage in the tar after centrifuging. The author also would like to remind the reader that these samples were treated by a laboratory decanter overnight. Therefore, the water percentages shown in these samples were the water which could not be separated by a centrifuge or a decantation method because of the emulsion state of water in tar. However, the water percentage of the tar after centrifuging meets the 3 per cent of the specification of creosote.

The specific gravity of the tar after centrifuging is 1.100 which meets the grade A of the specification. The specific gravity of the tar after centrifuging was lower than those of Samples No. 1 and No. 2. The same phenomena is shown for the results of the samples produced at the pilot plant. The reason is the reduction of the heavy oil over 355°C by the centrifuge.

The results of the distillation analysis also meets with the grade A of the specification except for the percentage of light oil. The distinguished mechanisms of this centrifuge are the reductions of light oil under 210°C and of heavy oil over 355°C, compared with the results of Samples No. 1 and No. 2 with the result of the tar after centrifuging.

The free carbon content in this tar is about the same as in Samples No. 1 and No. 2. The reason why the free carbon contents in the samples from the Red Lodge plant are larger than those of the samples from the pilot plant is probably because of the higher carbonization temperature used at the Red Lodge plant, besides the elimination of the combustion of light oil in the retort as mentioned before. That is, the higher carbonization temperature causes the higher free carbon. Therefore, whenever the Red Lodge plant is operated at around 1300°F carbonization temperature, the author expects that the free carbon content in the tar produced at the commercial plant will include about the same amount as the results shown in Table IX in the future.

In other words, the high coke residue in the tar after centrifuging, which does not meet the specification, can be reduced only by distilling off the heavy oil over 355°C, but not by the free carbon content in the distillation residue. It was felt by the author that it might be possible to reduce the heavy oil over 355°C by passing the crude tar through the centrifuge two or three times.

In order for the coke residue of the tar after centrifuging to meet the grade A of the specification (5 per cent), the percentage of the distillates up to 355°C has to be increased to about 87 per cent from the 60.61 per cent of the results shown in Table IX.

Calculations are as follows:

Assuming about 38 per cent for the free carbon content in the distillation residue,

$$\frac{(\text{per cent of distillation residue})(38)}{100} = 5$$

So,

the proposed per cent of distillation residue to meet the grade A of the specification =

$$\frac{(5)}{(38)}(100) = 13.15$$

Then,

the per cent of the distillate up to 355°C

$= 100 - 13.15 = 86.65 \doteqdot 87$ per cent.

However, though the results in Table IX show about a 10 per cent reduction of the distillation residue, the author believes that unfortunately this method of reducing the distillation residue by the centrifuge method mentioned above can not be reduced another 27 per cent.

Therefore, the author's recommendations for the designing of a distillation still at the commercial plant in Red Lodge, Montana, are as follows: First, the distillation still must ensure less possibility of water content than 3 per cent of the specification, even though the feed tar to the distillation still is separated from water by a centrifuge. Second, the distillation still should be effective to distill off the light oil to meet the 5 per cent of the specification. Third, in order to reduce the high coke residue percentage, it should be necessary to distill off the high portion of the feed tar.

5. Commercial creosote

A commercial creosote was analyzed and the results compared favorably with the specifications. One noticeable observation was high content of naphthalene, which easily crystallized at room temperature, in the fraction between 210 to 235°C. P.D.P. low-temperature tar has never shown crystallization of naphthalene or aromatic compounds in any fractions. Also, the small quantities of the fractions under 210°C and over 355°C means that the creosote has to be a distillate of coal tar.

B. Fractional distillation of light oil and tar

The experiments of fractional distillation of light oil and tar were practiced under vacuum of 60mm Hg. The results are shown in Figs. 32 and 33, respectively. The diagram of the apparatus is illustrated in Fig. 31.

1. Light oil

Fig. 32 shows the distillation curve of the light oil. The water percentage of this experiment is 10.25 per cent in volume which is a higher value than the results in Table IX. As shown in Fig. 32, the light constituents like benzene or toluene are under 5 per cent by volume (dry basis). According to the characteristics of low-temperature carbonization, the aromatic series should be very small in quantity; however, the light constituents of paraffin series should be in large quantity. This contradiction with the experimental results had to be caused by the combustion of some light oil in the retort.

After this light oil portion, the curve steadily increases with a boiling point increase. Therefore, this curve does not show any definite components, and the curve shows that the light oil is a mixture. The end point is 250°C under atmospheric pressure and the percentage at this point is about the same as the value of the percentage up to 355°C in Table IX.

2. Tar

The same methods as used on the light oil were used on the crude tar obtained from the gas absorption column at the P.D.P. pilot plant. As the results show in Fig. 33, the curve increases linearly with the temperature. The end point is approximately 355°C under atmospheric pressure, and the distillation residue is about the same amount as for the crude tar from the gas absorption column. Also, the values for each fraction in Table IX approximately correspond to the curve in this Figure. This increase of the tar fractional distillation curve also shows the mixed components in the crude tar just like the light oil.

Section II

Primary Designing of Coal Tar Distillation Still

I. Introduction

A great variety of coal tar distillation stills have been used up to the present time. Though these distillation stills are mainly divided into two classes, a batch process and a continuous process, the following designing is limited to the batch process. The reason is that the commercial plant of P.D.P. Processing, Inc. does not produce enough quantity of tar to construct a continuous distillation still.

In a batch process, many types of distillation stills have been used since the 19th century. These batch stills are also classified into two types, vertical and horizontal. Both the vertical and horizontal stills have a fractionation column, but in some cases it is attached on the top of the still, and in others it is separate from the still.

Although the vertical stills are usually used in Britain and on the European continent, the horizontal stills are customarily used for batch distillation in the United States. The author uses the horizontal batch still for the distillation of coal tar produced at the Red Lodge commercial plant in Red Lodge, Montana. As for the fractionation column, the author does not think it necessary because the main purpose of the distillation at the commercial plant is to produce creosote which has a wide boiling point range.

However, the single batch still has several disadvantages. One of the disadvantages is that the more the light oil constituents are vaporized, the more the residue becomes viscous, thereby causing local overheating of tar. The other disadvantage is the difficult operation in case of the foaming of tar during the distillation, which may cause the still to explode, or the tar to overflow into a condenser, either of which is dangerous.

The following descriptions will illustrate in detail each feature of the distillation still for the coal tar produced at the commercial plant of P.D.P. Processing, Inc. at Red Lodge, Montana.

II. Purposes

As mentioned in the previous section, the analyses of the tar after centrifuging, which produced at the commercial plant in Red Lodge, did not meet the grade A of the specification of the American Wood Preservers' Association.

The disadvantages were the high percentages of light oil and of the coke residue. Therefore, the purposes of the distillation still at the commercial plant have to be the reductions of light oil under 210°C and of the distillation residue over 355°C. Also, it would be necessary to ensure less possibility of water content in the commercial creosote.

III. Distillation Stills at the Red Lodge Commercial Plant

A. Capacity

The author arbitrarily chooses 100 ton of coal a day for the charring plant operation in the future. Considering the losses of tar at gas absorption columns and at a centrifuge, the author assumes 15 gals. of the crude tar produced from one ton of Brophy coal. This means that 1500 gals. of the crude tar a day will be produced at the commercial plant. This quantity is still not large enough to construct a continuous distillation still practiced at the present modern coking industry, but can be handled by a semi-batch still for short periods or for fairly long continuous operation.

Also, owing to the serious disadvantages of a single batch still as mentioned before, the author suggests setting up two stills for each fraction and one heat exchanger. The primary designs of these distillation stills are shown in Figures 34, 35, and 36.

B. Distillation stills

1. Crude tar

The crude tar passed through a centrifuge once is stored in a closed tank to prevent the increase of water content by weather. Or, the crude tar can be pumped directly into a heat exchanger. Since this entire distillation process uses the gravity flow of tar in the stills, the storage tank has to be higher than the height of the stills, and in case of pumping tar, the pressure of pumping has to be high enough to push tar through the heat exchanger and the stills.

2. Heat exchanger

The crude tar enters into the annular space of the heat exchanger at the back end. This heat exchanger is entirely immersed in the path of waste heat flue from No. 1 and No. 2 stills, and has a center tube in which the outgoing pitch from No. 2 still is passed. Therefore, not only the ingoing crude tar is warmed from outside by the waste heat flue, but it is also warmed from inside by the outgoing pitch which is reversely cooled down to the desirable temperature.

3. No. 1 still

Leaving the heat exchanger the hot tar enters the first still, flows down the cascade and along the still.

One of the risks during the distillation process of tar is "foaming" which the author frequently experienced at the laboratory experiments of tar distillation analyses. When the ingoing crude tar is used for condensing purposes, there is a tendency for the water in the crude tar to accumulate, forming "pockets" of water which occasionally pass forward to the still. As the temperature of the tar in the still is seldom below 200°C, it follows that, when the water comes into contact with the hot tar, "foaming" will occur. This difficulty can be eliminated by fixing in the vapour space of the No. 1 still a cascade, down which the crude tar must flow, in a thin layer, before it can enter the distilling tar.

Namely, the crude tar is not used for condensing the light oils, and accumulations of water are thereby avoided, and also the water contained in the crude tar is removed before it enters the body of hot tar in the still. The depth of the tar on the cascade favorably does not exceed half an inch, and the depth of the tar in the still generally one-third the diameter of the still.

By keeping the temperature of the vapours leaving the No. 1 still under 200°C, almost all of the light oil and water will be distilled off in this still.

4. No. 2 still

The tar leaves the No. 1 still from its front end and flows through a pipe into the front end of the No. 2 still, travels through a pipe in this still which extends to the back end, and is discharged there within the still (see Fig. 35). The tar now flows forward to the front of the No. 2 still, and collects in a pipe at the front end which carries it down to the heat exchanger.

A perforated steam pipe is fixed in the second still for steam distillation of high fractions between 270°C and 355°C, thereby causing the low temperature operation in this still.

5. Pitch

Leaving the No. 2 still at the front end the pitch is conveyed into the center tube at the front end. As the pitch is exchanging heat with the ingoing crude tar, it leaves at the back end of the heat exchanger.

The receiver of the pitch is a conveyor with a downward concavity at the center. This conveyor is sprayed with water at several points and the pitch on it is cooled till it reaches to the end of the conveyor. A scraper at the end of the conveyor scrapes off the pitch and discharges it into a car.

6. Furnace

No. 1 and No. 2 stills are heated by direct heat, but the heat exchanger is heated by waste gases from the first two stills. The supply of heat can, however, be regulated by movable dampers fixed over portholes in the curtain arch under the stills. The sliding dampers are operated from the front end of the still setting.

7. Steam boiler

At the end of the furnace, there is a steam boiler constructed similar to No. 1 and No. 2 stills. The steam boiler can be heated directly by the gas burner under the boiler while the tar distillation stills are not operated. When the distillation of tar is continued, this boiler is heated by hot waste gases from the heat exchanger chamber, and can be supplied extra heat by a gas burner under the boiler.

This boiler supplies steam not only to the entire plant operation, but also to No. 2 still for steam distillation.

8. Condensers

The fractions of distillates pass through tapering vapour pipes to rectangular condensers, fitted with "S" bend cast-iron pipes. After leaving the condensers the oils pass through cast-iron oil traps for separating foul gases. The working of the stills is controlled by thermometers at the front end, and a wide variety of fractions may be obtained by reducing the sliding dampers.

The steam pipes in the condensers are for the purposes of warming the condensers in case of plugging the condensing pipes or cleaning the pipes.

C. Construction of the distillation stills

The entire furnace has to be constructed of fire bricks inside and by regular bricks outside. No. 1, No. 2 stills, and heat exchanger are preferably made of stainless steel to prevent corrosion by sulfur in tar, and the steam boiler is made of regular steel.

The three iron bars across the stills and boiler are to prevent the explosion of the stills. For inspection purposes, the front end plate of the still is bolted to the still, and may be conveniently removed when desired. The back end plate is welded to the still. All connections from one still to another are fixed outside at the front end of the stills. They are not submitted to the heat of the flue gases, hence there is no risk of carbonization or blocking in these connections.

D. Operating conditions

The following are the estimations of the operating conditions of the above distillation stills.

1. Working temperatures:

No. 1 still	210°C
No. 2 still	260°C
Temperature of ingoing tar	100°C
Temperature of pitch at outlet	150°C

2. Amounts of yields

Assuming 100 tons of coal per day for the feeding coal to the charring plant, and considering the results of the tar after centrifuging at the charring plant in Red Lodge, the amounts of yields distilled by this distillation stills are approximately as follows:

Working period	24 hrs. a day
Feeding crude tar	63 gals. per hour
Aqueous liquid	2 gals. per hour
Light oil	39 lbs. per hour
Creosote	442 lbs. per hour (52 gals. per hour)
Pitch	72 lbs. per hour

ACKNOWLEDGEMENTS

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The author thanks the Engineering Experiment Station of Montana State College for the opportunity it presented to work on this project. The author acknowledges aid and suggestions supplied by the entire staff of the Chemical Engineering Department of Montana State College. Special thanks are extended to Robert Lengemann and many workers whose efforts and aid in the operation of the plant and experiments promoted completion of this work.

To Asahi-Kasei Chemical Industry Company, the author extends his gratitude for much helpful grant to complete this thesis.

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APPENDIX

APPENDIX

TABLE I

AVERAGE VALUES OF COAL ANALYSES IN PERCENTAGES
(Wet Basis)

Coal		Moisture	Volatile Matter	Fixed Carbon	Ash
Spitsburgen Coal (Norway)		1.61	37.18	53.39	7.82
Knife River Lignite Coal (North Dakota)	old sample	8.61	37.3	43.95	10.14
	new sample	24.75	27.07	40.19	7.99
Routt Coal (Colorado)		8.08	36.00	48.73	7.19
Utah Coal (Utah)		2.53	42.00	50.07	5.40
Montana Coal & Iron Co. (Red Lodge, Montana)		4.97	30.38	53.97	10.68
Janskovich Coal Co. (Red Lodge, Montana)		6.58	33.0	49.20	11.22
Brophy Regular Coal (Red Lodge, Montana)		7.62	33.85	50.35	8.18
Brophy Fine Coal (Red Lodge, Montana)		15.88	31.50	46.07	6.55
Brophy Fine Coal - crushed (Red Lodge, Montana)		12.35	32.22	48.38	7.05
Brophy Regular Coal sampled from carload	No. 1	6.49	36.86	51.39	5.26
	No. 2	7.55	35.29	52.22	4.94
	No. 3	6.98	35.33	51.06	6.90
	No. 4	5.83	36.22	49.86	8.09
	No. 5	6.24	35.86	52.34	5.56
	No. 6	6.62	36.00	50.49	6.89
	No. 7	6.66	35.61	50.63	7.10
	No. 8	5.86	41.02	45.04	8.08
	No. 9	7.30	35.80	49.67	7.23