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[54] **TWO STAGES OF COKING TO MAKE A HIGH QUALITY COKE**
3 Claims, 1 Drawing Fig.

[52] U.S. Cl. 208/50, 208/53, 208/131
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[50] Field of Search 208/50, 53, 131

[56] References Cited
UNITED STATES PATENTS

2,775,549	12/1956	Shea, Jr.	196/52
2,922,755	1/1960	Hackley, Jr.	208/39

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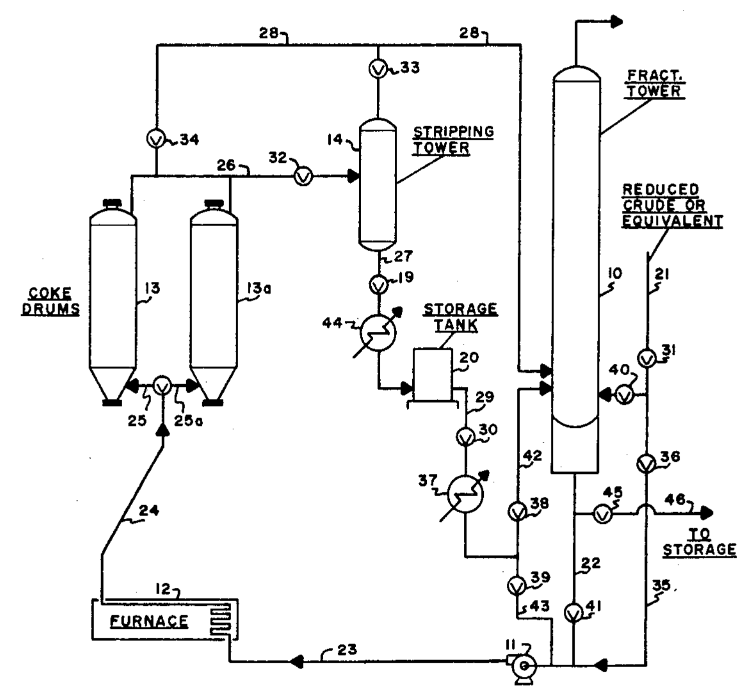
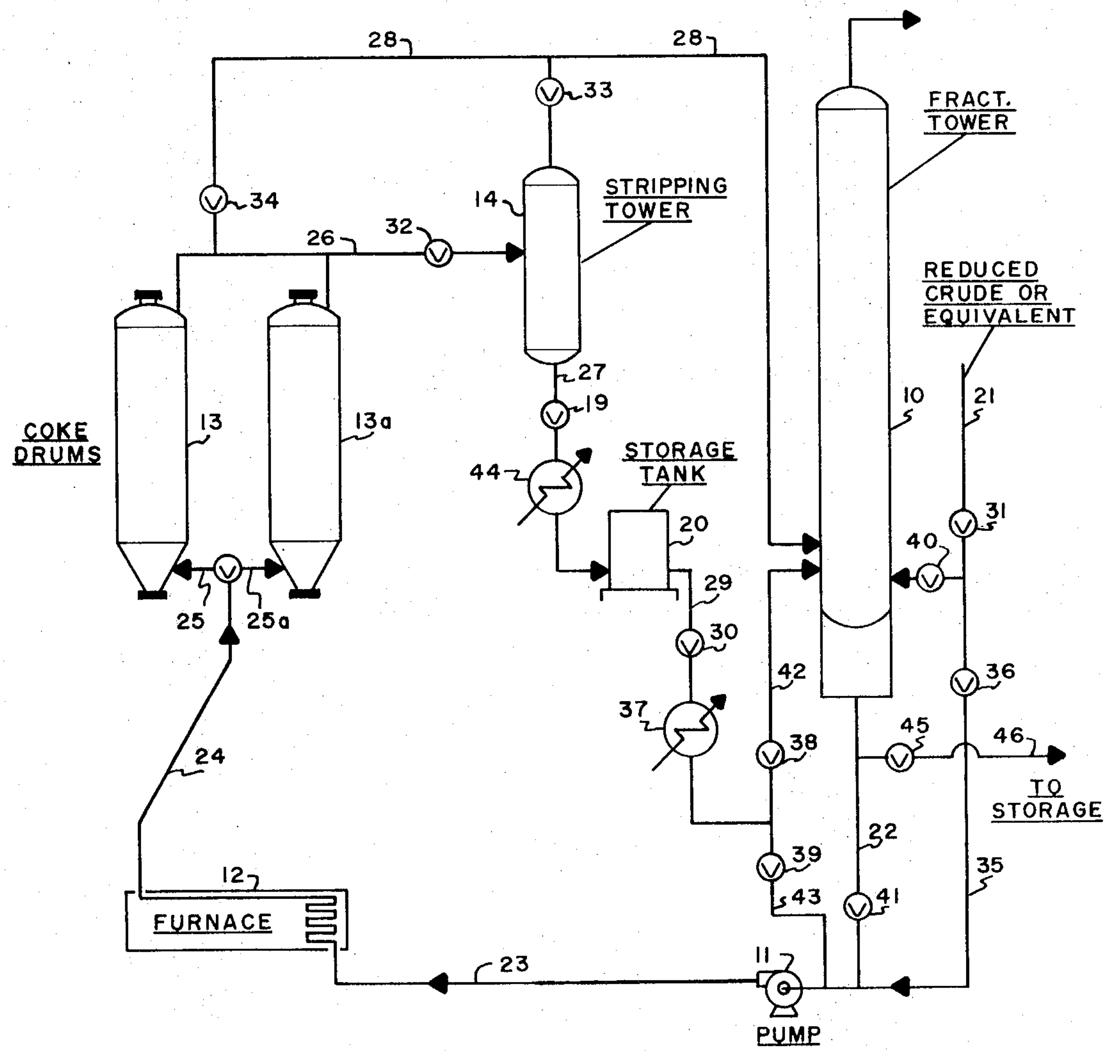
ABSTRACT: The coking process disclosed herein provides a method for producing high quality petroleum coke which is particularly suitable for use in manufacturing electrothermic graphite electrodes. A high-boiling gas oil fraction is obtained from the overhead products produced during the coking of a petroleum oil residuum. This high-boiling gas oil fraction is segregated during the manufacture of regular or average quality petroleum coke and is subsequently coked in a separate coking operation under delayed coking conditions of time, temperature and pressure to produce a superior quality petroleum coke.





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TWO STAGES OF COKING TO MAKE A HIGH QUALITY COKE

BACKGROUND OF THE INVENTION

This invention relates to a method of producing a high quality petroleum coke which, when used as an aggregate in the manufacture of electrothermic graphite electrodes, will produce electrodes Process," a low coefficient of thermal expansion (CTE), improved electrical resistivity and other properties which will enhance the performance of large diameter graphite electrodes in electric steel furnaces. Petroleum coke is usually produced by coking a high-boiling petroleum residuum such as a reduced or topped crude oil or vacuum reduced crude oil, in a variety of coking methods. One of the most common methods employed currently is the so-called "-delayed coking" process which is described in an article by R. J. Diwoky "Continuous Coking of Residuum by the Delayed Coking Process", in Refiner and Natural Gasoline Manufacturer, Vol. 17, No. 11, Nov. 1938. The present invention involves the use of this type of coking operation.

The manufacture of high quality or "premium" petroleum coke suitable for use as an aggregate raw material for the manufacture of graphite electrodes involves the selection of certain selected petroleum-derived feedstocks which are used as the feed to the delayed coking process. One of the earliest disclosures of a process for producing this type of coke appears in U.S. Pat. No. 2,775,549-Shea. The two most economic and commercially feasible methods for producing coke in accordance with that process are described in examples VIII and IX of the patent which teach the use of a gas oil fraction obtained from a Mid-Continent asphaltenic or naphthenic crude oil as a feedstock for catalytic and/or thermal cracking and recovery of high-boiling "bottom fractions" or tars from these operations which are then coked under carefully controlled conditions in the delayed coking process. A similar and equivalent process is disclosed in U.S. Pat. No. 2,922,755 which also describes the differences between regular petroleum coke produced from petroleum residues and "-premium" coke. Another process involving the utilization of overhead products from the delayed coking petroleum residues is disclosed as U.S. Pat. No. 3,089,074. A distillate fraction derived from the delayed coker overhead is thermally polymerized and is then combined with the residuum feed which is then sent to the delayed coking operation. While this type of operation is designed to increase the coke yield of the original feedstock, it will have little effect, if any, upon the ultimate quality of the coke produced by this process.

OBJECTS OF THE INVENTION

It is an object of the present invention to provide a method for producing a high quality or "premium" coke from petroleum fractions which previously have not been utilized solely as a feedstock to the delayed coking process. It is a further object of the invention to provide a method for increasing the commercially available supply of high quality petroleum coke. It is an additional object of the invention to produce high quality petroleum coke by a "blocked out" delayed coking operation employing as a feedstock a heavy gas oil fraction derived from a petroleum residuum which itself will not produce premium coke.

SUMMARY OF THE INVENTION

The present invention consists of a method for producing high quality petroleum coke from a petroleum residuum, such as a topped or reduced asphaltenic or naphthenic crude oil or vacuum-reduced crude oil of this type which, in and of itself, will not produce high quality or premium petroleum coke suitable for use as a carbon aggregate in the manufacture of large diameter electrothermic graphite electrodes. THe petroleum residuum is first heated in a suitable heat exchanger to a coking temperature, after which it is coked under conditions of delayed time, temperature and pressure, to produce coke and distillate products. These distillate products are fractionated and there is recovered therefrom a heavy gas oil fraction at least 80 percent of which has a boiling point above 700° F. This heavy gas oil fraction is then coked in a separate or "-blocked out" coking operation under delayed coking conditions of time, uniform temperature and pressure. After the coking drum or vessel is about two-thirds full of coke, the feed to the coking vessel is stopped and switched to another vessel to continue the operation and the coke is removed from the first vessel by any of a variety of procedures, such as hydraulic decoking, which are well-known to those skilled in the petroleum refinery art. The resulting coke is then calcined at a temperature of up to 2,600° F. to reduce its volatile content to less than 0.5 percent by weight. The calcined material is then crushed and sized and is an excellent material when employed as a carbon aggregate in the manufacture of high quality electrothermic graphite electrodes which are used in electric steel furnaces.

Sample electrodes prepared for CTE determination by the method disclosed in U.S. Pat. No. 2,775,549 (except for calcination of the coke to 2,280° F.) have a CTE (measured over the temperature range 32° to 167° F.) of $6.0 \times 10^{1}7$ or less and the coke will produce large electrothermic electrodes which have advantageously low CTE and electrical resistivity properties.

DETAILED DESCRIPTION OF THE DRAWING

The foregoing objects of the invention and summary thereof may be further illustrated by a detailed description of the invention as supplemented by the drawing which depicts schematically a flow diagram of a preferred embodiment of the invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

A reduced or topped asphaltenic or naphthenic petroleum oil, or vacuum reduced oil of this type is conveyed from the crude oil tower (not shown), from which it leaves at a temperature of about 600° F., through line **21** and valves **31** and **40** (valve **36** being closed) into the bottom portion of a fractionating tower **10** which is also receiving hot overhead or distillate products from the coking vessel as later described herein. The hot reduced crude oil together with small amounts of high-boiling materials which are not distilled overhead from the fractionating tower are conveyed through line **22** and valve **41** to a pump **11** and thence through line **23** to a heat exchange furnace **12** of conventional design. The feed conveyed to the coker from the furnace through line **24** is at a temperature within the range of 900° to 950° F. By means of a valve, the feedstock is conveyed into coke drums **13** or **13***a* by line **25** or **25***a*. Two-coke drums are normally employed in refineries using the delayed coking process because while one drum is being filled with the hot residuum and producing coke and overhead products, the other drum is being cooled and the coke removed therefrom by hydraulic or other means well-known to those skilled in the art. THe hot feed entering the coke drum undergoes decomposition (cracking), polymerization and aromatization. As these chemical processes proceed to completion, petroleum coke is formed and gradually fills the coke drum while the distillate products produced by these chemical reactions are conveyed out of the drum. With valve **34** closed and valve **32** open, these distillate products are conveyed to a stripping tower **14** where a high-boiling gas oil faction, at least 80 percent of which has a boiling point (atmospheric conditions) above 700° F., is collected. If required, the stripping tower **14** may be equipped with a reboiler or jacketed for recirculating of heat exchange media necessary to maintain the desired bottom temperature. Also, a partial condenser can be used as a reflux for maintaining the top stripping temperature. The lighter boiling products from the stripping tower are conveyed through valve **33** and line **28** to the fractionating tower **10** from which the lower boiling products including gas, gasoline and light gas oil are recovered. The high-boiling gas oil faction which collects in the stripping tower **14** is conveyed through line **27** and valve **19** to a heat exchanger **44** into a storage tank **20** to be processed in a separate or "blocked out" delayed coking operation.

If it is not desired to admit the heated reduced crude oil or equivalent into the bottom portion of the fractionating tower **10**, this unit may be bypassed by closing valve **40** and opening valve **36** and pumping the reduced crude, through a heat exchanger (not shown) if necessary, through line **35**, pump **11** and line **23** to the heat exchange furnace **12**.

To produce high quality or premium petroleum coke according to this invention from the high-boiling gas oil fraction which has been collected in storage tank **20**, the reduced crude oil or equivalent feed is shut off by valve **31** and the gas oil fraction is conveyed through line **29** and valve **30** to a heat exchanger **37** and thence either to the lower zone of fractionating tower **10** through valve **38** and line **42** or, alternatively, bypassing the fractionating tower by closing valve **38** and opening valve **39** and conveying it through line **43** to pump **11** and through line **23** to the heat exchange furnace **12**. The heavy gas oil fraction is uniformly heated in the furnace to the temperature up to 950° F., preferably 925° to 945° F., and then conveyed to one of the coke drums **13** or **13***a* through line **24**. The heavy gas oil is passed into the coke drum under uniform temperature and pressure conditions, where it undergoes decomposition (cracking), polymerization, aromatization and ultimately coke formation. The lower boiling products produced from these reactions leave the top of the coke drum and are returned to the fractionating tower through open valve **34** and line **28**. In this operation, the stripping tower **14** may be omitted from the circuit and valves **32, 33** and **19** will be closed. In the fractionating tower most of the cracked distillate products will be fractionated as overhead products and some higher boiling material will be recycled to the coke drum through line **22** and valve **41**. After the coke drum is about two-thirds filled with coke, the valve between the drums is switched and the feed is admitted to the second drum while the first drum is being cooled internally by high temperature, high pressure steam after which the coke is removed from the drum preferably by hydraulic means which are well-known to those skilled in the art. The coke yield, based on the fresh feed from tank **20**, will be within the range of 15 to 35 percent, depending on the coking cycle. When a sample of this coke is calcined at a temperature sufficiently high so that the residual volatile matter is about 0.1 percent and the coke is ground to flour size (52 percent –200 mesh) and is used to make test graphite electrodes, the resulting electrodes will have a CTE of about 4.0×10^{17} (over the temperature range 32° to 167° F.) and is an excellent material to produce carbon aggregate in the manufacture of high quality large electrothermic graphite electrodes.

If the refining operation does not contemplate the use of a stripping tower **14** to collect the heavy gas oil fraction which is used as the feedstock to produce premium coke in accordance with this invention, the entire cracked, distillate product from coking the reduced crude oil or equivalent can be sent to the fractionating tower **10** which is operated at a bottom temperature sufficiently high so that at least 80 percent of the heavy gas oil which collects at the bottom of the unit has a boiling point of about 700° F. In such case, the reduced crude or equivalent will bypass the fractionating tower **10** and, with valves **40** and **41** closed and valves **31** and **36** open, will be sent directly to the furnace **12** and thence to one of the coke drums. This material can then be sent to storage tank **20** by closing valve **41** and opening valve **45** and conveying the material through line **46**.

While I have described my invention specifically in terms of the foregoing preferred embodiment, it should be understood that it is limited only by the scope of the appended claims.

What is claimed is:

1. In a process for producing high quality petroleum coke from a petroleum residuum which will not produce said coke directly which comprises removing from the residuum those components which readily form an insoluble phase upon heating the residuum 650°–1,000° F., coking the remaining tar in a quiescent pool, and recovering a high quality petroleum coke therefrom; the improvements consisting of the following combination:

a. heating said residuum to a coking temperature;
b. coking said heated residuum under conditions of delayed time, temperature, and pressure to produce coke and distillate products;
c. fractionating said distillate products to recover therefrom gas, gasoline, light gas oil, and a heavy gas oil fraction at least 80 percent of which has a boiling point about 700° F.; and
d. coking the heavy gas oil fraction from step (c) in a subsequent and separate coking operation under delayed coking conditions at a uniform temperature between 925° to 950° F. and underpressure.

2. A method according to claim **1** wherein said petroleum residuum is derived from a topped or reduced asphaltenic or naphthenic crude oil.

3. A method according to claim **1** wherein said petroleum residuum is derived from a vacuum reduced asphaltenic or naphthenic crude oil.

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