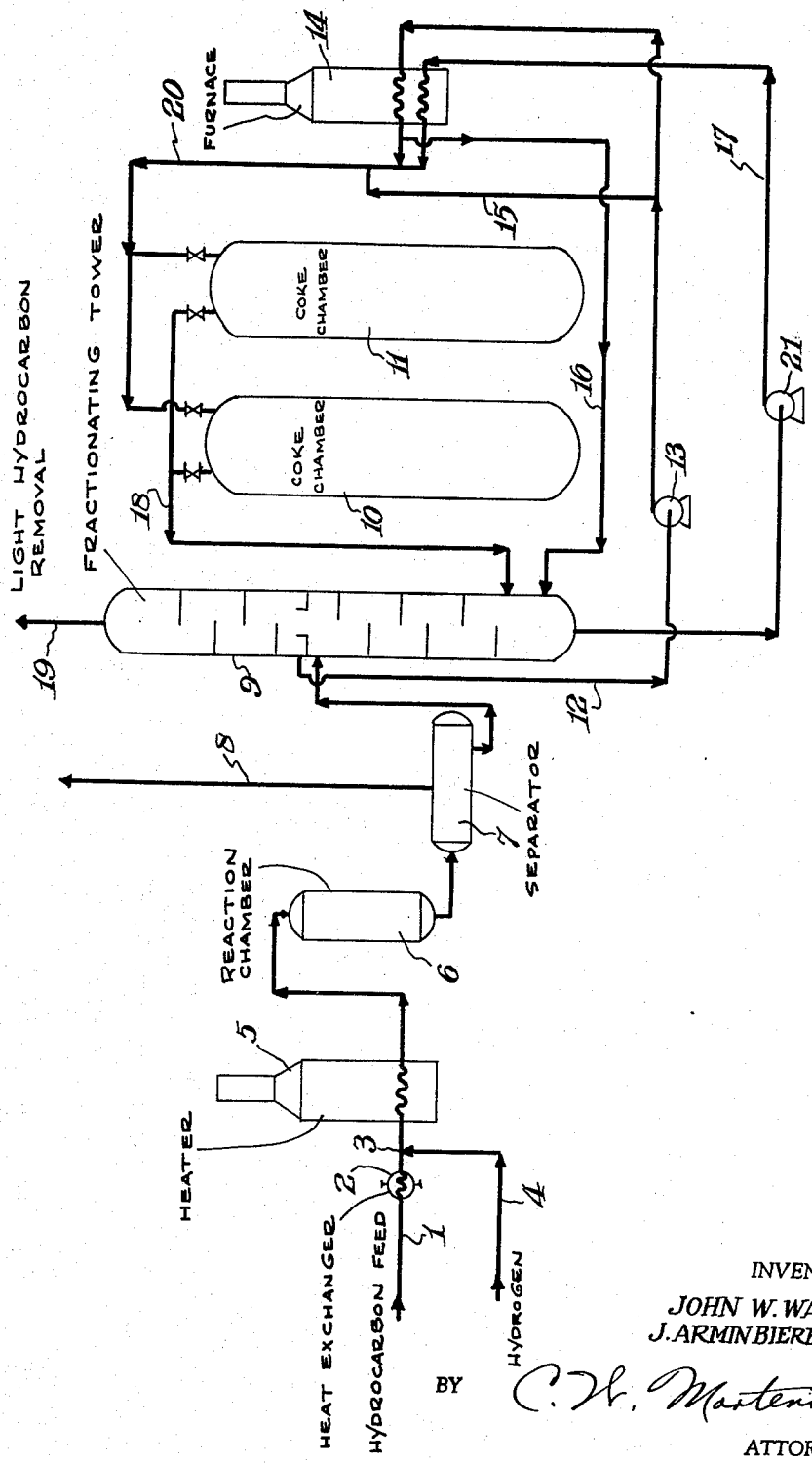
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COKE PRODUCTION FROM PETROLEUM STOCKS

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INVENTORS
JOHN W. WARD &
J. ARMIN BIERBAUM

BY C. H. Martenson

ATTORNEY

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COKE PRODUCTION FROM PETROLEUM STOCKS

John W. Ward and J. Armin Bierbaum, McPherson, Kans., assignors to General Carbon and Chemical Corporation, Robinson, Ill., a corporation of Delaware

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This invention relates to the production of coke and more particularly, it relates to the production of high quality coke.

There is an increasing demand for coke of high quality in a number of industries, as, for example, in the metallurgical industries. Such cokes must be purified carefully, the chief impurity to be removed being sulfur. In using stock stemming from petroleum the sulfur content of the starting product may be as high as 8% or more. For the production of high quality carbon for use in certain metals, metal alloys and atomic work, the sulfur content of the coke must be essentially negligible. Methods for producing high quality coke heretofore have been time consuming and expensive. A rapid, effective and low-cost method is needed.

An object of this invention is to produce a high quality coke by an efficient dependable and low-cost method. A further objective is the provision of a method for reducing the sulfur and metals content of material to be coked and controlling the coking so that a high quality coke is continuously produced. A further objective is the removal of sulfur and metals from the charge stock prior to coking in a manner integrated with the coking step. A still further objective is the provision of a method for coking whereby the coking is continuously controlled. These and other objectives will appear hereinafter.

The objectives of this invention are accomplished by treating the hydrocarbon being fed with hydrogen under hydrogenation reaction conditions, fractionating the resultant product, and controlling the temperature of the stock being fed into the coke chamber by quenching or by-passing a portion of the stock feed. By the processes of this invention thermal conversion of a variety of hydrocarbon oils and the like to gasoline or lighter fractions is accomplished while producing a valuable high quality coke. This invention will be further understood by reference to the following discussion and to the figure.

The figure is a flow diagram showing different processes of this invention.

Referring to the figure, a hydrocarbon feed is fed through line 1 through a heat exchanger 2. After being heated, it is mixed at 3 with hydrogen coming from feed line 4. The pressure of the hydrogen gas may vary between about 200 to about 5,000 p.s.i.g. Further heating is accomplished by passing the hydrogen-hydrocarbon mixture through heater 5, the temperature being attained varying from about 400° F. to about 1,000° F. dependent upon the material being processed and the results desired. The mixture is then passed through a reaction chamber 6 containing a catalyst such as a cobalt molybdenum catalyst. Hydrogenation along with some thermal cracking occurs therein. Sulfur is converted to volatile sulfur compounds such as hydrogen sulfide which are removed in separator 7. Unused hydrogen and waste products are taken out through line 8, the hydrogen being recycled by feeding it to line 4 and mixing it there with fresh hydrogen.

It should be noted that this pretreating of the hydrocarbon stock removes impurities other than sulfur. For example, it removes objectionable nitrogen compounds and metallic compounds. As to the removal of nitrogen compounds, compounds such as pyrrole, quinoline and pyridine are converted to hydrocarbons and ammonia. Along with or as an alternate to the hydrogen treating step, there can be used other desulfurizing and demetalizing agents, such as the hydrogen fluororide-boron trifluoride complex or metallic sodium. These agents, among others, assist in the removal of the impurities.

In the hydrogenation process, the pressure may vary appreciably and may be as high as 200 atmospheres and above. Usually, the pressures are in the range from about 200 lbs. per sq. in. to 1,000 lbs. per sq. in. with the temperatures in the range from about 300° F. to 1,200° F. In general, the temperatures of the reaction are somewhere around 700° F. to 1,000° F. The rates of feed vary widely, but are generally in the range from 0.5 to 4 volumes of feed per volume of catalyst per hour. The amount of hydrogen introduced per mol of feed is in the range from about 1.0 to about 20 mols of hydrogen per mol of feed.

With the desired hydrogenation effected, the stock is further prepared for coking to get high quality coke by passing it to fractionating tower 9. In the tower the light hydrocarbon products are removed through line 19. If the stock that is being used is easily susceptible to thermal break down, charging to the coke chambers may take place with only furnace temperature control. These chambers 10 and 11 are chambers having coil temperatures varying from about 800° F. to about 1,100° F. Pressures within the chambers vary from about 15 p.s.i.g. to about 200 p.s.i.g. and the temperatures are about 750° F. to about 900° F. Proper coking temperatures must be attained to get high quality coke. With refractory stocks this is accomplished by cooling the stocks being fed.

As shown in the diagram one way to accomplish the desired cooling or temperature control is to pass a portion of the light feed from tower 9 through feed line 12 and pumping it by pump 13 partially through furnace 14, quenching the furnace 14 effluent with that portion of the by-passed feed through line 15. The material passing through line 15 may be cooled prior to blending it with the effluent but inasmuch as it is already colder than the effluent, quenching is generally accomplished by introducing a controlled amount of the colder material into the hotter stream. The heavy feed is taken from the bottom of tower 9 and pumped by pump 21 through line 17 to the furnace 14. The heavy feed can also be used as quench oil.

Another way in which control is effected is to feed a portion of the light material coming from the furnace 14 back into the tower 9, by-passing the coke chambers by way of pipe 16. This reduces the temperature within the coking chambers. For example, the temperature control or quenching may be obtained by sending a portion of the effluent from furnace 14 through pipe 16 to tower 9. Pipe 16 is valved adjustably so that the flow of furnace effluent to the coking chambers maintains the temperature balance within the chamber and so that the flow of feeds from tower 9 through lines 12 and 16 cooperate therewith in the control. In other words, the material flowing through line 20 to the coking chamber is controlled both as to amount and temperature and proper coking temperatures are attained with the attendant production of high quality coke.

By such methods as quenching the streams or by-passing the coke chambers the rates of cracking can be kept high so that the process is commercially feasible. This is particularly advantageous in handling of stocks that

are refractory and in the handling of stocks that are to be coked to extinction.

The coke is intermittently removed from the unused filled coking chamber by conventional means. The vapors from the coking chambers are led through feed line **18** back into the fractionating tower **9** at the bottom thereof for separation into proper furnace feeds and desired overhead products.

This invention is further illustrated by reference to the following examples which are not limitative being given only for illustrative purposes, percentages being by weight.

Example I

An asphaltic material, derived from a typical North American crude and having a sulfur content of 5% by weight and an ° API of 5, is fed into the system of this invention through feed line **1** for pretreatment with hydrogen, fractionation and coking. Using quenching line **15**, the products obtained were as follows:

Product:	Amount in percent
Butane and lighter products	12
Debutanized gasoline (° API–55)	25
Coke gas oil (° API–28)	24
Coke	39
	100

The coke had a sulfur content in the range of about 0.01% to about 0.2% and it was extremely low in metal contaminates and nitrogen. The gas oil can be readily converted into additional coke by recycling it to extinction.

Similar results are attained with reduced crude and virgin crude, and high quality cokes are also attained by using by-pass line **16**.

Example II

A heavy catalytic cycle oil (° API–24) derived from a Mid-Continent crude was processed in the manner described above to yield the following products:

Product:	Amount in percent
Butane and lighter products	30
Debutanized gasoline (° API–55)	42
Coke	28
	100

The heavy cycle oil had a sulfur content of approximately 2%. The coke had a sulfur analysis running from about 0% to about 0.2%. It was free from undesirable metals and from nitrogen.

The rates of feeds will depend upon the apparatus used and the products desired. In cycling to extinction a variety of charges, the process of this invention can be used to process without difficulty unlimited amounts of feed stocks producing a high grade coke that is uniform in its absence of impurities.

The catalyst may be selected from a wide variety of materials. The cobalt-molybdenum catalyst referred to above and that catalyst on aluminum oxide are frequently used. Metallic oxides of chromium, molybdenum, zinc, tungsten may be used alone or with other oxides and the sulfides of these metals may also be used. Dehydrogenation effects may also be accomplished and extenders or carriers for the catalysts, such as silica, magnesia and alumina may be employed. To illustrate somewhat further the catalyst types, mention is made of nickel sulfide-alumina, nickel sulfide-molybdenum sulfide, tungsten sulfide-nickel sulfide, platinum-alumina, nickel oxide-molybdenum oxide-alumina, cobalt thiomolybdate-alumina-silica and molybdenum sulfide on activated alumina. The catalysts used are not poisoned by sulfur or its compounds and all types of sulfur compounds are removed. That is, the process of this invention converts sulfur compounds, whether they be in mercaptan, disulfide, olefinic, or thiophenic in nature, to readily removable, highly volatile materials. The final products contain little or no sulfur.

This is true irrespective of the starting product. The hydrocarbon oil feeds that can be used include the various heavy crudes commercially available, light reduced crudes, heavy reduced crudes, atmospheric and vacuum crude oil bottoms, heavy gas oils, pitch, asphalt, high boiling synthetic hydrocarbon oils, and the various petroleum residues or mixtures of these various sources. If desired preformed coke may be added. The principles of this invention may also be applied to fluidized systems. The feed rates of the various materials will, of course, depend not only on the substances being processed but upon the apparatus being used. To illustrate, the feed from the furnace **14** varies greatly with the feed stock. In Example I, the combined feed was about twice the fresh feed whereas in Example II, it was about seven times the fresh feed. Regardless of the stock being used by use of the quenching or by-passing steps of this invention the feed rates and temperature conditions are readily controlled to produce a friable coke that is readily removed. Most important, it is a high quality, pure coke irrespective of the feed stock processed.

With certain of these stocks some impurity removing agent other than, or in combination with, hydrogen is used. For example, carbon monoxide, carbon dioxide, chlorine, steam producer gas, coke oven gas, phosphoric acid or ammonia may be used. Special metal removing agents such as boron trifluoride complexes are used. Further, oxidation-reduction systems may be used. For example, an active metal such as sodium is usually converted to sodium sulfide which is removed as a precipitate or a deposition and the hydrocarbon portion is liberated. For example, the metal impurities accumulate on catalysts surfaces from which they are periodically removed. Normally, oxygen and air are not used in the process of this invention but may be used to support combustions or for aeration purposes. The sulfur-containing gas can be used for fuel or sulfur may be recovered therefrom.

The various light products obtained by the processes of this invention such as butane or gasoline have the obvious uses as fuel. The high quality coke that is produced is used to considerable advantage in the production of electrode carbon in demand in the electrochemical industries as, for example, in the production of aluminum. The pure coke is also used in lime burning in the manufacture of soda ash, for making phosphorous, in the manufacture of calcium carbide and in other uses.

One of the advantageous features of this invention involves the pretreatment of the stock to be coked to purify it prior to coking. This step is dove-tailed into the coking step so that a continuous, well-integrated process is attained. The coking process of this invention may be applied to feed stocks which have been separately or previously treated elsewhere, but for greatest economy the controlled coking of this invention will be used in continuous conversions of stocks directly to high-quality cokes.

Another outstanding feature is the control of the temperatures in the coking ovens. This is done by quenching certain streams or parts thereof going to the coke chamber or by-passing such streams around the coke chamber to the fractionating tower. The temperatures within the chamber are lower than usually prevailing and they are kept within a more narrow range. For example, the coke chambers are normally kept within about 750° F. to about 900° F. In the coking the expelling of volatiles is uniformly effected so that a solid, uniform coke that is readily removed from the chamber is obtained. The lower temperatures and greater control provide for greater uniformity of the coke product. This is highly important in many of the uses of coke, such as those mentioned above, for reproductivity purposes.

While the invention has been disclosed herein in connection with certain structural embodiments and certain procedural details, it is clear that changes, modifications or equivalents can be used by those skilled in the art; accordingly, such changes within the principles of this invention are intended to be included within the scope of the claims below. For example, a single coil furnace could be used instead of the double coil furnace shown in the figure.

We claim:

1. A process for producing coke of electrode quality from petroleum stocks which comprises pretreating the said stock prior to coking to remove impurities by treating said stock in the presence of sulfur removing agents to convert sulfur compounds present in the stock to volatile sulfur compounds; removing said compounds; passing the resultant purified mixture to a fractionating tower; removing light hydrocarbon fractionated products from said tower, leaving behind residual light and heavy fractions; passing said light and heavy fractions from said tower to a furnace for further heating; passing a portion of said light fraction coming from said furnace back to said tower; then passing the remainder of said heated fractions under controlled conditions to a coking chamber, thereby controlling the temperature in the coking chamber within a narrow range; and coking the said fractions.

2. A process for coking a petroleum stock to produce coke of electrode quality which comprises treating the said stock in the presence of a sulfur removing agent, thereby converting sulfur compounds present in said

stock to volatile sulfur compounds; removing said volatile sulfur compounds to form a substantially sulfur-free product; passing said purified product to a fractionating tower; removing volatile, light hydrocarbon products therefrom leaving behind residual light and heavy fractions; passing said residual heavy fraction resulting from said fractionation tower to a furnace for further heating; passing said residual light fraction from said fractionation tower partially to said furnace for further heating and partially to a quench line; combining the feed of the resultant effluent from said furnace with the said quench line feed; feeding the said combined stream to a coking chamber and coking.

3. A process in accordance with claim 2 in which the volatile products resulting from the said coking are passed to the said tower for fractionation.

4. A process in accordance with claim 2 in which the coking produces a coke having from about 0% to about 0.2% by weight of sulfur.

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