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3,687,840

DELAYED COKING OF PYROLYSIS FUEL OILS
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12 Claims

ABSTRACT OF THE DISCLOSURE

Process for delayed coking of pyrolysis fuel oil wherein the operation includes the following steps, alone or in combination:

- (a) addition of sulfur into the pyrolysis fuel oil prior to introduction into a soaking tank,
- (b) maintenance of the pyrolysis fuel oil at above 450° F. for at least 5 minutes in the soaking tank before it is passed to the coking heater, and
- (c) operation of the heater coil outlet and the coke drum at a pressure of not less than 40 p.s.i.g.

The use of the above steps in the delayed coking process avoids the formation of plugs in the system and facilitates the preparation of high quality cokes from pyrolysis fuel oils.

Optionally, a quench system may be employed in the vapor line leaving the coke drum, particularly where a highly reactive feedstock is used, to prevent vapor phase coking.

BACKGROUND OF THE INVENTION

The delayed coking of petroleum residual oils is well established in the petrochemical industry, providing the maximum return from residual oils in that it yields both coke and more desirable liquid and gaseous products, such as liquified petroleum gas, gasoline and gas oil. It has come to have a more particular importance since it has also been found to be an excellent route to the production of premium grade or needle coke, useful in the production of large graphite electrodes, from certain selected clean feedstocks high in aromatics content.

While the use of pyrolysis fuel oils as feedstocks for the conventional delayed coking process has been described, it has been found that in industrial practice such use has been attended by significant and material disadvantages. In particular, it has been found that various components of the delayed coker unit become plugged up by deposition of coke and/or polymer, thereby rendering the plant nearly inoperable or so reducing the operating efficiency as to render the process industrially unattractive by increasing greatly the operating costs of the delayed coking process. Thus, it has been found that plugs of coke or polymer are formed in the fractionator bottom section, the heater coil, the transfer line to the coke drums and the vapor lines leaving the coke drums.

SUMMARY

The present invention relates to and has for its objects the production of a high quality coke from highly reactive pyrolysis fuel oils which are difficult to process. More particularly, the present invention relates to a new and improved process for the delayed coking of pyrolysis fuel oils to permit the attainment of high on-stream efficiency or trouble-free operation.

It has been found that the disadvantageous plugging by the deposition of coke and polymer heretofore encountered in the delayed coking of pyrolysis fuel oils can be avoided by the inclusion of certain additional features in

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the delayed coking process. According to the present invention, efficient and practical production of high quality coke from pyrolysis fuel oils can be effected by the inclusion, alone or in combination, of the following steps in the delayed coking process:

- (a) addition of sulfur to the pyrolysis fuel oil prior to its introduction into a soaking tank,
- (b) maintenance of the pyrolysis fuel oil at above 450° F. for at least 5 minutes in the soaking tank before it is passed to the coking heater and,
- (c) operation of the heater coil outlet and coke drum at a pressure of not less than 40 p.s.i.g.

A further optional feature may be the employment of a quench system in the vapor lines leaving the coke drums.

By the inclusion of one or more of these steps in the delayed coking process, the formation of plugs at the vulnerable points in the delayed coking unit is substantially eliminated.

BRIEF DESCRIPTION OF THE DRAWINGS

The figure is a simplified schematic flow diagram of an embodiment of the invention.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The feedstock which is charged to the delayed coking unit in the practice of the present invention is a pyrolysis fuel oil. Pyrolysis fuel oils are the residual heavy black oils boiling above pyrolysis gasoline, that is, boiling above about 375° to about 425° F., which are produced together with olefins in the pyrolysis of liquid hydrocarbon feedstocks. Such residual oils are well known and are described for example, in U.S. Pat. Nos. 3,326,796 and 3,451,921 and in the patents and publications referred to in said patents.

In carrying out the process of the present invention, sulfur is incorporated into the feedstock prior to delivery of the pyrolysis fuel oil into a soaking tank not provided in a conventional coker. The sulfur can be added to the pyrolysis fuel oil in the form of elemental sulfur or in the form of a suitable organic sulfur compound, such as a mercaptan. In whatever form it is employed, the quantity employed must be sufficient so that sulfur is present in the pyrolysis fuel oil in an amount not less than about 30 parts per million and preferably in the range of from about 100 to 200 p.p.m.

In order to facilitate the solution of elemental sulfur in the oil, it is desirable to add the sulfur to the oil at a temperature of from about 100° to about 300° F., preferably at from 150° to 200° F. Advantageously, this can be effected by dissolving sulfur in a slipstream and thereafter blending the resulting solution back into the feed.

The pyrolysis fuel oil is then passed to the soaking tank where it is subjected to a "soaking" treatment comprising holding the oil in the vessel at a temperature of from about 450° to about 600° F., preferably at approximately 500° F., for a period of from about 5 minutes to about 120 minutes, usually for a period on the order of from about 15 to about 25 minutes.

At the end of this period the thus treated pyrolysis fuel oil is mixed with a recycle stream in the volumetric ratio of recycle to fresh coker feed of from about 0:1 to about 5.0:1 and then passed to the coker heater. Here the feedstock is heated rapidly to a temperature of about 850° F. prior to passage to the coke drum. The coker heater outlet and the coke drum are maintained at a pressure of not less than 40 p.s.i.g., advantageously of from about 75

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p.s.i.g. to about 150 p.s.i.g., thereby maximizing the proportion of feed which is in the liquid phase during the period it is in the heater coil.

Following passage through the coking heater, the pyrolysis fuel oil is delivered to the coking drum where the formation of coke occurs. The coke is formed and discharged in accordance with any of the procedures commonly employed in the art except that, as noted above, the coke drum during the coking period is maintained at a pressure of not less than 40 p.s.i.g.

In accordance with an optional practice, the coke drum vapor may be subjected to quenching by means of a quench system located in the vapor line leaving the coke drum. This feature precludes vapor phase coking and serves to flush the vapor line free of any coke which may already have formed.

The invention will now be more specifically described with reference to the embodiment thereof illustrated in the drawing. The drawing has been simplified to facilitate the description thereof and hence various processing expedients such as valves, pumps and the like are not specifically shown therein. It is to be understood that the embodiment of the drawing is only illustrative of the invention and that the scope thereof is not to be limited thereby.

Referring now to the drawing, a pyrolysis fuel oil, such as the heavy high boiling fractions obtained in the cracking of petroleum distillates in the presence of steam to produce olefins, is charged to the unit via line 10. A slipstream of this feed is passed through a pot 2 containing elemental sulfur. The slip-stream dissolves sufficient sulfur so that upon blending with the main stream, the sulfur content in the feed will be from about 30 to about 200 p.p.m. The sulfur-containing pyrolysis fuel oil is then passed through heat exchanger 11 to effect heating thereof by indirect heat transfer with a heavy oil fraction, as hereinafter described, and through line 13 into soaking tank 4 wherein the pyrolysis fuel oil is held at a temperature of approximately 500° F. and at a pressure of from about 1 to about 150 p.s.i.g. for a period of 5 minutes to 120 minutes. Vapor from soaking vessel 4 passes into the fractionator 12 through line 3 where it mixes with vapor from the coke drum 18. In the fractionator, the high boiling fractions of the coke drum vapor condense and are withdrawn from fractionator 12 through line 14 where, as recycle, they are admixed with the heat treated oil withdrawn from soaking tank 4 through line 5 and passed to line 34.

The combined feed in line 34 is introduced into a coking heater 15, of a type known in the art, operated so as to produce an outlet temperature of from about 825° to about 1000° F., ordinarily at from about 825° to about 950° F. This heater coil is also operated at an outlet pressure of not less than about 40 p.s.i.g., preferably at a pressure of from about 75 to about 150 p.s.i.g. In a manner conventionally employed in the art to prevent premature coking in a coking heater, the feed to the coil is maintained at a high liquid velocity. As the oil is heated, the temperature and pressure profiles in the heater will produce partial vaporization of the feed, thereby increasing the flowing velocity and preventing the coking problems caused by a slow moving feed. However, in this case it is most desirable to keep as large a fraction of this feed in the liquid phase as practical consistent with high liquid turbulence. Sometimes controlled amounts of steam may be introduced into the coking heater 15 at appropriate places to obtain the required high velocity.

The heated feed is withdrawn from the coker heater 15 through line 17 and introduced into coke drum 18, of a type known in the art, wherein the heavier components of the feed are converted to coke and lighter components. The coking drums are operated at a pressure of not less than 40 p.s.i.g., preferably between about 75 p.s.i.g. and 150 p.s.i.g. and at a temperature of from

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about 800° to about 925° F., preferably from about 825° to about 900° F. The coke is withdrawn from coking drum 18 through line 19 after the drum is filled. During this period of withdrawal, the alternate coke drum 18A is on-stream to be filled with coke.

In the optional embodiment wherein a quench system is employed, the vapor withdrawn from coke drum 18 through line 21 is quenched to below 750° F., preferably to from about 600° to about 700° F. by means of a quenching system comprising the light distillates withdrawn from fractionator 12 through line 31 and brought into contact with the vapor from coker drum 18 by passage through line 32.

The effluent from the coker drum is separated in combination fractionator 12 into various products of different boiling ranges and usually comprises gasoline, light gas oil, heavy gas oil, and recycle. The gasoline is taken overhead and when condensed has an end point between 350 and 425° F. The light gas oil which boils above the gasoline is taken as a side cut and has an initial boiling point between 325° F. and 400° F. and an end point between 450° F. and 675° F., but usually about 650° F. The heavy gas oil is taken as a higher boiling side cut and has an initial boiling point between 425° F. and 650° F., usually about 625° F., and an end point between 500° F. and 750° F. The end point of the heavy oil is determined by the ratio of recycle to fresh coker feed charged to the coker heater. The initial boiling point of the recycle is between 475° F. and 725° F. and contains all the higher boiling components in the coker effluent.

The heavy gas oil, withdrawn from fractionator 12 through line 22, is cooled in heat exchanger 11 by indirect heat transfer with the feed in line 10 and further cooled in heat exchanger 23 to a temperature suitable for inducing the required recycle into fractionator 12, generally to a temperature of from about 350° to about 600° F., by indirect heat transfer with a suitable coolant, for example, boiler feed water. A portion of this stream of cooled heavy gas oil from heat exchanger 23 is introduced into the fractionator 12 through line 25 or 26 at a controlled rate to induce a volumetric ratio recycle to fresh coker feed of from about 0.0:1 to about 5.0:1. The total recycle is comprised of the heavier fraction of the heavy gas oil introduced through 25 or 26, the condensed heavy oil vapors from the coke drums introduced through line 21, and the condensed heavier vapors introduced through line 3, the condensation being induced by direct contact with the cooled heavy gas oil fraction as well as lighter reflux from the top of the tower. The net make of heavy gas oil from the coking unit is taken from heat exchanger 23 and sent through line 27 to storage.

Numerous modifications of the invention are possible within the spirit and scope thereof. Thus, for example, the feed may be treated to effect vaporization of material below the end point of the light gas oil to be recovered in the delayed coking process in apparatus other than the coker combination fractionator or the soaking tank. The feedstock can be fractionated separately in a distillation tower to take out lighter fractions and in such case where reboiler holdup is of sufficient duration there would in effect occur a soaking treatment equivalent to that which takes place in the soaking tank. In like manner, retention of the oil in a separate vessel under pressure and at a sufficient temperature would likewise provide a treatment equivalent to that which takes place in the soaking tank. Such alternative embodiments are to be considered as embraced within the term "passing the sulfur-containing pyrolysis fuel oil to a soaking zone wherein said oil is held at a temperature and for a period of time sufficient to polymerize highly unsaturated components present in said oil." Similarly, the various heat transfer steps can be effected otherwise than as hereinabove described, for example, the feed to the combination fractionator may be heated in the convection section of the coking heater or even another heater.

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The invention is further illustrated by the following example but the scope of the invention is not to be limited thereby.

EXAMPLE

A pyrolysis fuel oil derived from the steam cracking of naphtha for the production of olefins, having the properties set forth in Table I is coked in accordance with the conditions of Table II.

TABLE I

Sp. grav. -----	1.0404
Visc., S.U.S. at 100° F. -----	53.6
Conradson carbon wt. percent -----	9.44
5% boiling point, ° F. -----	390
Diene value -----	9.3

TABLE II

Line:	Temp., ° F.	Pressure, p.s.i.g.	Flow rate, #/hr.
10-----	60-----		34.0
13-----	500-----		34.0
3-----	500-----		18
5-----	500-----		16
14-----	650-----		28.6
17-----	850-----	90	44.6
21-----	700-----	90	56.9
32-----	60-----		19.1

The recycle oil from line 14 from the bottom of fractionator provides a recycle ratio of 1.8:1 by weight, based on fresh feed.

The fractionator 12 is operated at an overhead temperature of about 200° F. and a pressure of 0 p.s.i.g. In addition to the overhead gas product, the following liquid products are recovered, based on total feed.

TABLE III

Component	Wt. percent on feed	Lb./hr.
Gasoline (C ₅ -356° F.)-----	10.6	3.6
Kerosine (356-446° F.)-----	30.9	10.5
Gas oil (+446° F.)-----	35.0	11.9
Total liquid product-----	76.5	26.0

Coke is produced at the rate of 6.8 lbs./hr. (19.9 wt. percent based on fresh feed) and has the following properties:

TABLE IV

Ash (wt. percent) -----	0.0
Sulfur (wt. percent) -----	0.02
Volatile matter (wt. percent) -----	6.2
Fixed carbon (wt. percent) -----	93.8
Apparent density, lb./cu. ft. -----	62.7

The above procedure is repeated employing as feedstock the pyrolysis fuel oils having the properties set forth in Table V.

TABLE V

Gravity, specific at 60/60° F.-----	1.0703	1.1752
Viscosity:		
SUS at 140° F.-----	575.8	
SUS at 210° F.-----	93.2	
SFS at 250° F.-----		93.5
Conradson carbon, wt. percent-----	16.3	31.1
Sulfur, wt. percent-----	1.6	2.77

The coke produced from the above feedstocks is of the same general order of properties as that produced from the feedstock of Example I.

In accordance with the present invention, pyrolysis fuel oil feeds are subjected to a delayed coking procedure

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without occurrence of adverse plugging in the delayed coking unit to provide an excellent yield of coke. With low sulfur, highly aromatic pyrolysis fuel oils, the coke produced is of premium grade. When it is calcined and fabricated into an extruded electrode and graphitized, it is characterized by a satisfactory longitudinal coefficient of thermal expansion of less than $1.1 \times 10^{-6}/^{\circ}\text{C.}$ (measured between 30-100° C.)

We claim:

1. A delayed coking process for the production of petroleum coke which comprises dissolving sulfur, said sulfur being in the form of elemental sulfur or a mercaptan, in a pyrolysis fuel oil, in an amount of not less than 30 nor more than 200 parts per million, passing the sulfur-containing pyrolysis fuel oil to a soaking zone, wherein said oil is held at a temperature and for a period of time sufficient to polymerize highly unsaturated components present in said oil, passing the treated oil to a heating zone wherein the treated oil is heated to a coking temperature at a pressure of not less than 40 p.s.i.g., then passing it to a coking zone, maintaining a liquid body thereof in said zone at a coking temperature and converting it to coke.

2. A process according to claim 1 wherein the sulfur is dissolved in the pyrolysis fuel oil by heating.

3. A process according to claim 2 wherein the sulfur is added in the form of elemental sulfur.

4. A process according to claim 2 wherein the sulfur is added in the form of an organic sulfur compound.

5. A process according to claim 1 wherein the pyrolysis fuel oil is held in the soaking zone at a temperature of from about 450° to about 600° F. for a period of from about 5 to about 120 minutes.

6. A process according to claim 1 wherein the pyrolysis fuel oil leaving the heating zone is at a temperature of from about 825° to about 1000° F. and at a pressure of from about 40 p.s.i.g. to about 300 p.s.i.g.

7. A process according to claim 1 wherein the coking zone is maintained at a pressure of not less than about 40 p.s.i.g.

8. A process according to claim 7 wherein the coking zone is maintained at a pressure of from about 40 to about 150 p.s.i.g.

9. A process according to claim 8 wherein the coking zone is maintained at a temperature of from about 825° to about 980° F.

10. A delay coking process for the production of petroleum coke from pyrolysis fuel oil which comprises dissolving sulfur in the form of elemental sulfur or a mercaptan in a pyrolysis fuel oil in an amount of not less than 30 nor more than 200 parts per million by subjecting the mixture of said oil and sulfur to a temperature of from about 100° to about 300° F., passing the sulfur-containing oil to a soaking zone wherein said oil is held at a temperature of from about 450° to about 600° F. for a period of from about 5 to about 120 minutes, passing the treated oil to a heating zone where said oil is heated to a temperature of from about 825° to about 1000° F. at a pressure of from about 40 p.s.i.g. to about 300 p.s.i.g., then passing it to a coking zone where it is coked at a temperature of from about 825° F. to about 980° F. and at a pressure of from about 40 p.s.i.g. to about 150 p.s.i.g.

11. A delayed coking process for the production of premium grade coke which comprises dissolving sulfur, said sulfur being in the form of elemental sulfur or a mercaptan, in a pyrolysis fuel oil in an amount of not less than 30 nor more than 200 parts per million, passing the sulfur-containing pyrolysis fuel oil to a soaking zone wherein said oil is held at a temperature and for a period of time sufficient to polymerize unsaturated components present in said oil, passing the treated oil to a heating zone wherein the treated oil is heated to a coking temperature at a pressure of not less than 40 p.s.i.g., then passing it to a coking zone, maintaining a liquid body thereof in said zone at a coking temperature and converting it to coke, and subjecting vapor emitted from the coking zone to

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quenching prior to condensation and recycling thereof.

12. In a delayed coking process for the production of petroleum coke which comprises subjecting a pyrolysis fuel oil to a preheating step, passing said preheated oil to a heating zone where it is raised to coking temperature and then coking said pyrolysis fuel oil, the improvement which comprises dissolving sulfur in said fuel oil, said sulfur being in the form of elemental sulfur or a mercaptan, in an amount of not less than 30 nor more than 200 parts per million, prior to the preheating step.

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