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FAST THERMAL CRACKING OF HEAVY CARBONACEOUS MATERIALS

Filed May 6, 1963

2 Sheets-Sheet 1

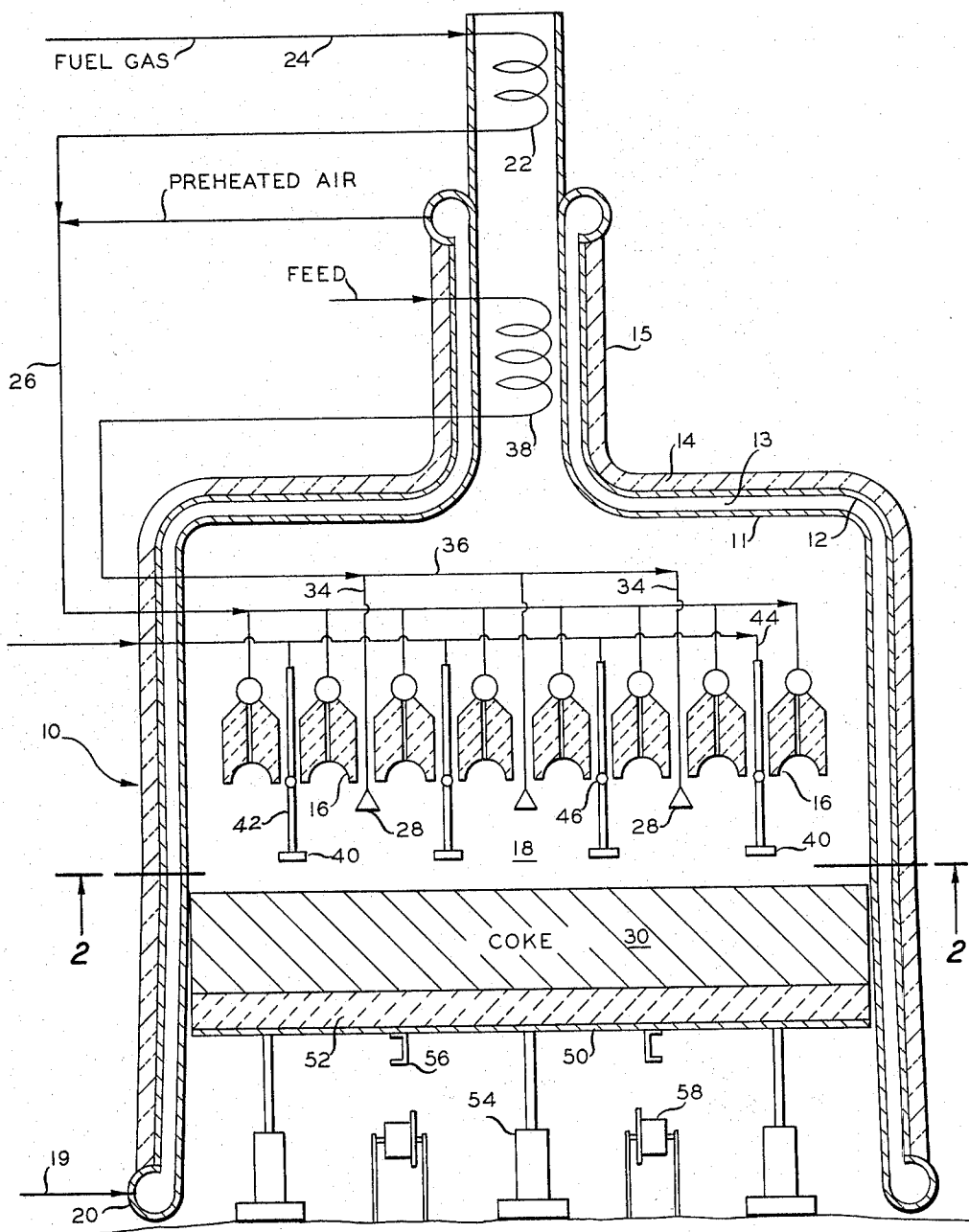


FIG. 1

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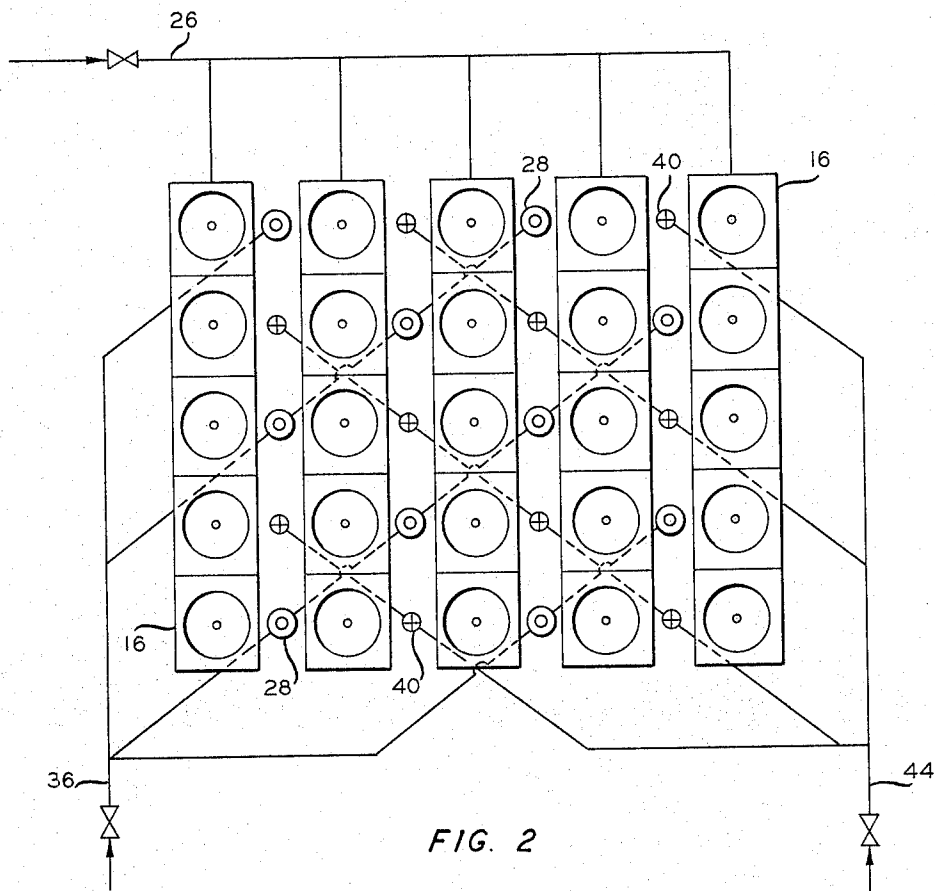


FIG. 2

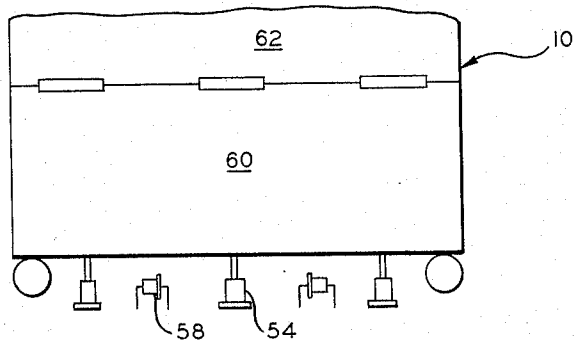


FIG. 3

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FAST THERMAL CRACKING OF HEAVY CARBONACEOUS MATERIALS

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15 Claims. (Cl. 208-46)

This invention relates to a process and furnace for cracking heavy carbonaceous materials to gaseous and liquid hydrocarbons and to coke.

Fluid catalytic cracking processes normally require residence times of 1.5 to 10 minutes and coking operations require longer residence times. These relatively slow reaction rates enhance carbon formation, polymeric condensations, and dehydrogenation with lower ultimate yields of gasoline and other liquid products. This invention is concerned with a process and furnace capable of supplying the energy of activation and over-all enthalpy requirements for cracking heavy carbonaceous materials, such as heavy petroleum oil, in a short reaction time, whereby the reaction rate rather than chemical equilibrium controls product distribution.

Accordingly, it is an object of the invention to provide a process and furnace for cracking heavy carbonaceous materials, such as petroleum oils, to gasoline and other valuable lighter hydrocarbons and producing a calcined coke. Another object is to effect faster cracking of heavy carbonaceous feed stocks than is possible with conventional furnaces and processes. A further object is to produce higher yields of gasoline and distillates in thermal cracking of hydrocarbons than are conventionally obtained. It is a still further object to employ reactor conditions whereby high sulfur, heavy oils are converted to low sulfur coke. It is also an object of the invention to provide a cracking process and furnace of high heating efficiency. Other objects will become apparent to one skilled in the art upon consideration of the accompanying disclosure.

A broad aspect of the invention comprises a cracking furnace including an enclosed heating chamber having an outlet for cracked gaseous products, a plurality of downwardly directed radiant burners closely spaced substantially above the bottom of the chamber and connected with an air-fuel supply, means among the burners for supplying a liquid carbonaceous feed downwardly toward the bottom of the chamber, and means for quenching the hot cracked products. The process of the invention comprises directing radiant heat at oil cracking temperatures onto a bed of coke in an enclosed cracking zone, simultaneously spraying liquid carbonaceous feed onto the coke while at said temperature so as to crack the feed to lighter hydrocarbons and coke, and quenching and recovering the lighter hydrocarbons and coke from the cracking zone.

The radiant heat is supplied by burning a near theoretical air-fuel mixture in a radiant burner provided with a concave ceramic face to produce a temperature of at least 2,000° F. and up to about 3,200° F. The air-fuel mixture is burned on the face of the burner which is concave so as to concentrate the radiant heat and direct the same toward the bed of coke. One type of burner which is particularly effective in the furnace of the invention is the Selas burner manufactured by the Selas Corporation of America, Dresher, Pennsylvania.

Materials suitable for cracking and coking in accordance with the invention include petroleum oils, such as heavy gas oil, oil tars, pitches or residua from the aforesaid materials, and mixtures of these raw materials. In general any semi-solid to solid bituminous material which

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can be liquefied below the incipient cracking temperature are suitable feeds for cracking; however, heavy petroleum oils boiling above about 500-600° F. are the preferred feeds.

A more complete understanding of the invention may be had by reference to the accompanying schematic drawing of which FIGURE 1 is a vertical section thru a furnace constructed in accordance with the invention; FIGURE 2 is a horizontal cross section of the furnace of FIGURE 1 taken on the line 2-2; and FIGURE 3 is a fragmentary end view of the furnace of FIGURE 1.

Referring to FIGURE 1, a furnace 10 comprises an inner shell 11 and an outer shell 12 forming a jacket and providing a fluid circulating space 13. Shell 12 is covered with insulation 14. Outlet 15 in the top of the furnace provides an effluent line for cracked products which are passed to conventional separation and recovery equipment not shown. A plurality of closely spaced premix radiant burners 16 (or ceramic faced ribbon burners) are suitably supported in cracking chamber 18 with their radiant faces directed toward the bottom of the chamber.

Air line 19 connects with ring 20 to preheat air for a near theoretical premix, such as air and natural gas, the fuel gas being preheated in heat exchanger 22 in outlet 14, heater 22 being in fuel supply line 24. The preheated premix passes thru line 26 to a series of spaced-apart burners 16 where it is burned on the burner faces to produce radiant heat for the process. Burners 16 may be directly mounted on the burner manifold as shown.

A plurality of feed sprays or injection nozzles 28 are dispersed among burners 16 so as to spray liquid feed over the whole bottom area of chamber 18 onto coke bed 30. Injection nozzles 28 are connected by individual lines 34 with feed line 36 which passes thru heat coil 38 in outlet line 15. This arrangement provides for suitable preheating of the feed just before injecting same into the furnace. A suitable feed preheating furnace may be utilized in conjunction with the arrangement shown where necessary to render the feed sufficiently fluid to pump the same thru the system shown. The feed may be preheated up to incipient cracking temperature before being charged to the furnace.

Quenching is effected by means of primary fog nozzles 40 located close to the coke bed, such as approximately 2 to 4 inches and, preferably, about 2½ inches above the coke. These nozzles are designed to produce a flat radial spray pattern and are mounted in line 42 connected with the common quench line 44 delivering liquid water at a supply pressure of 400 to 500 p.s.i. A secondary system of quench nozzles 46 is located above the primary system of nozzles 40 in line 44. The nozzles 46 are also fog nozzles but they are designed to produce jets of fog in the space between burner banks 16.

The bed of coke 30 that accumulates with time is supported on a reinforced steel plate 50 covered with insulation 52. The surface of the coke bed is maintained at an average elevation of about one foot (in the range of 10 to 14 inches) below the face of the burners 16 by means of hydraulic jacks 54. The whole coke bed is slowly oscillated in a vertical plane by means of the hydraulic jacks with a sufficient amplitude to prevent any firm attachment to the inner wall 11 of the furnace 10. Progressive lowering of the coke bed 30 as operation proceeds causes the supporting plate 50 and attached rails 56 to make contact with the support rolls 58. At this stage the operation is terminated long enough to discharge the coke from the furnace. With the hydraulic jacks 54 fully retracted, the wheel-supported coke bed is transported

on the rails thru hinged door 60 in FIGURE 3 in the end wall 62 of furnace 10 to a point outside the furnace. Depending on end use, the coke bed may be broken up and pulverized by conventional means or it may be pushed off the plate in a manner to preserve its structure as a solid slab of dense coke.

The lower section of the wall of furnace 10 is outwardly flared on all four sides as at 64 to facilitate lowering of supporting plate 50 without binding unduly around the periphery of the coke slab with the wall 11. The flare starts just above the maximum upper level of the coke.

The inside wall 11 is preferably fabricated from 310 stainless steel which will withstand temperatures up to 2000° F. Insulating material 52 consists of a high purity calcium aluminate cement or similar insulating refractory material.

It is also feasible to control the distance of the radiant surfaces of the burners from the top of the coke bed by moving an assembly of burner-feed spray-water nozzles up and down in the furnace as the coke thickness changes, by supporting structure not shown.

In FIGURE 2 a preferred arrangement of burners, feed injection nozzles and fog quench nozzles is shown. The burner banks are preferably positioned about 8 inches apart to provide both an ample concentration of heat on the coke bed on the bottom of the cracking chamber and also to allow the vapor product to escape from the reaction section. A principal requirement is the provision of a high enough heat flux to perform the cracking step in a minimum of time, such as about 1.0 to 4.0 seconds.

Radiant burners can be focused so that radiant energy is absorbed directly on the uppermost coke layer. This means that the walls receive little direct radiation, a feature that considerably reduces the materials of construction problem relative to conventional coking operations.

In addition to the utilization of an air-fuel gas mixture in radiant burners, the invention encompasses the alternate use of an oxygen-fuel gas mixture in a radiant-type burner specially designed for mixtures of this kind.

FIGURE 3 needs little explanation, it being presented to illustrate one method of removing the coke mass from the furnace, i.e., thru hinged door 60.

The invention has a number of advantages over prior art operation in

(1) Heating a reacting coke bed surface by radiation;
(2) Heating droplets of hydrocarbon feed by impingement upon hot coke, with the result that the lower molecular weight cracked products substantially escape further pyrolysis by vaporization;

(3) Returning the heavier or normally coke-forming hydrocarbons to the coke surface, by means of the water fog immediately above the coke bed, where they may be further cracked to desirable end products, particularly in the form of dense coke, ethylene and propylene;

(4) The thermal emissivity of the water and hydrocarbon vapors increasing with path length, with the result that second stage in situ heating and pyrolysis can be achieved; reaction kinetics permit thermal conversion of 60 percent of the intermediate boiling range paraffins while degrading only about 1 percent of the originally produced ethylene;

(5) That steam rates necessary for the production of about 95 percent olefin concentration in the C₂ and C₃ fractions can be generated in situ, without outside steam plant investment;

(6) That a much shorter reaction time is achieved than in a delayed coker or in a catalytic coking unit; and

(7) That a greater concentration of ethylene and propylene is achieved in pyrolytic step effluent, with the result that a lower equipment investment is achieved.

To illustrate the invention, the following example is presented. This example is not to be construed as unneces-

sarily limiting the invention but merely as illustrating the same.

Heavy paraffinic residuums are a suitable source of light olefins when processed in our apparatus. In this example the feed employed is a vacuum fuel oil having the following characteristics:

A.P.I. gravity	15.8
Distillation (vac), percent:	
I.B.P.	860
5	985
10	1020
20	1075
30	Crk
Carbon residue (Ramsbottom), wt. percent	8.2
Viscosity, SUV sec.	730

The feed, preheated to 750° F., is sprayed directly onto a radiant-ly-heated solid coke bed by means of spray nozzles into a furnace constructed substantially in accordance with furnace shown in the drawing. These spray nozzles are selected to provide the smallest droplets consistent with stable operation and a spray pattern affording good coverage. The air-natural gas premix burners have nominal 12-inch diameter radiant cups and are spaced approximately 12 inches above the coke. Near maximum ethylene production is achieved by rapid quenching in the zone immediately above the coke to provide an average hydrocarbon temperature of about 550° F. in the zone from about 2½ to 3½ inches above the coke. This rapid quench is provided by water fog issuing in a thin flat radial pattern from fog nozzles utilizing water delivered at a pressure of about 600 p.s.i.g. Quench water in the amount of 0.8 to 1.4 pounds per pound of hydrocarbon feed shock chills the products of the very fast reaction occurring at the coke surface which is apparently maintained at near 1350° F. In addition, this quench serves to condense heavy ends, particularly of the 900+° F. range, and returns these, the major sources of coke, to the hot coke surface. The vapors rising from the coke bed progressively absorb a part of the radiant energy, even while passing thru the quench zone immediately above the coke. This results in a very steep temperature gradient with reaction conditions being reached at the 9 to 12 inch levels which result in further pyrolysis, particularly of the gasoline thru heavy gas oil fractions. An additional ethylene yield amounting to at least 37 percent of the total ethylene yield can be realized from this zone. A second quench level served by jet type fog nozzles directed along the spaces between the burners quenches this secondary pyrolysis reaction and also cools the burner gases that curl up around the edges of the burners.

Reaction conditions minimize secondary reactions that yield paraffins. As a result, olefin concentrations in the C₂ and C₃ fractions run as high as 95 percent and the following over-all yield is representative:

	Weight percent yield
N ₂	60.0
CO ₂ , CO	12.5
H ₂	0.2
C ₁	1.8
C ₂	8.6
C ₃	4.1
C ₄	3.5
Gasoline	3.5
400-750	1.6
750-900	1.0
900+° F.	0.3
Coke	2.4
Losses	0.5
	100.0

Certain modifications of the invention will become apparent to those skilled in the art, and the illustrative details disclosed are not to be construed as imposing unnecessary limitations on the invention.

We claim:

1. A furnace for cracking hydrocarbons which comprises an enclosed heating chamber having an outlet for cracked gaseous products in its upper section and an impervious flat bottom for supporting a bed of coke during operation; a plurality of downwardly directed radiant burners spaced substantially above the bottom of said chamber connected with an air-fuel supply line, each burner being constructed with a ceramic concave face for burning a premix of air and fuel thereon; spray means among said burners connected with a hydrocarbon feed line for spraying a liquid hydrocarbon feed downwardly toward the bottom of said chamber; and quenching means connected with a quench feed line for quenching hot cracked products at a level intermediate said burners and the bottom of said chamber.

2. The furnace of claim 1 wherein said burners are disposed in parallel rows closely spaced so as to direct radiant heat over substantially the entire bottom of said chamber, said spray means comprises a plurality of spray nozzles closely spaced among said burners so as to spray liquid hydrocarbon over substantially the entire bottom of said chamber and said quenching means comprises spray nozzles spaced to spray quench fluid over substantially the entire horizontal cross-sectional area of said chamber.

3. A furnace for cracking hydrocarbons which comprises in combination

(1) an enclosed heating chamber having an outlet in its upper section for cracked gaseous products and a flat bottom supporting a bed of coke;

(2) a plurality of downwardly directed radiant burners at an intermediate level in said chamber, each said burner having a concave ceramic face for burning a premix of air and fuel thereon and said burners being spaced apart and disposed to direct radiant heat over substantially all of the bottom of said furnace;

(3) a plurality of feed injectors disposed at a level below said burners and connected with a feed line so as to direct feed over said bottom; and

(4) a plurality of quench sprays disposed at a level below said feed injectors and connected with a quench-fluid supply line so as to disperse quench fluid over substantially all of the horizontal cross-sectional area of said furnace.

4. The furnace of claim 3 wherein said bottom is movable vertically within said furnace and including means for moving same up and down therein.

5. The furnace of claim 3 wherein said feed injectors and said quench sprays are suspended on their respective feed lines extending downwardly between said burners from supply lines extending across the upper portion of said furnace.

6. The furnace of claim 5 including secondary quench fluid dispensers disposed in the feed lines to said sprays at a higher level.

7. The furnace of claim 4 including a door in the lower section of the end of said furnace for moving said bottom laterally out of the furnace.

8. The furnace of claim 4 wherein the lower section of the walls thereof are flared outwardly to avoid excessive binding of said bottom and coke thereon as same is lowered during operation.

9. A process for cracking heavy hydrocarbon oil comprising directing radiant heat from radiant burners at oil cracking temperatures onto an impermeate bed of coke in an enclosed cracking zone; simultaneously spraying oil onto said coke while at said temperature so as to crack said oil to lighter hydrocarbons and produce more coke; spraying quenching fluid directly into the cracked hydrocarbons above said bed of coke; and recovering said lighter hydrocarbons from above said bed of coke.

10. The process of claim 9 wherein said radiant heat is produced by burning a near theoretical air-fuel mixture adjacent a ceramic concave surface to produce a temperature of at least 2000° F.

11. The process of claim 9 including the steps of calcining said coke and removing the calcined coke.

12. The process of claim 11 wherein oil feed is periodically cut off and radiant heating is continued to effect the calcining.

13. The process of claim 9 including the step of controlling the distance between said burners and the top of said coke bed as coke is built up thereon.

14. The process of claim 13 wherein said coke bed is lowered to maintain said distance substantially the same.

15. The process of claim 9 wherein the distance between said burners and the top of said coke bed is maintained in the range of 10 to 14 inches and a water quench is dispersed in a generally flat radial spray pattern from a plurality of sprays at a level in the range of 2 to 4 inches above the top of the coke bed.

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