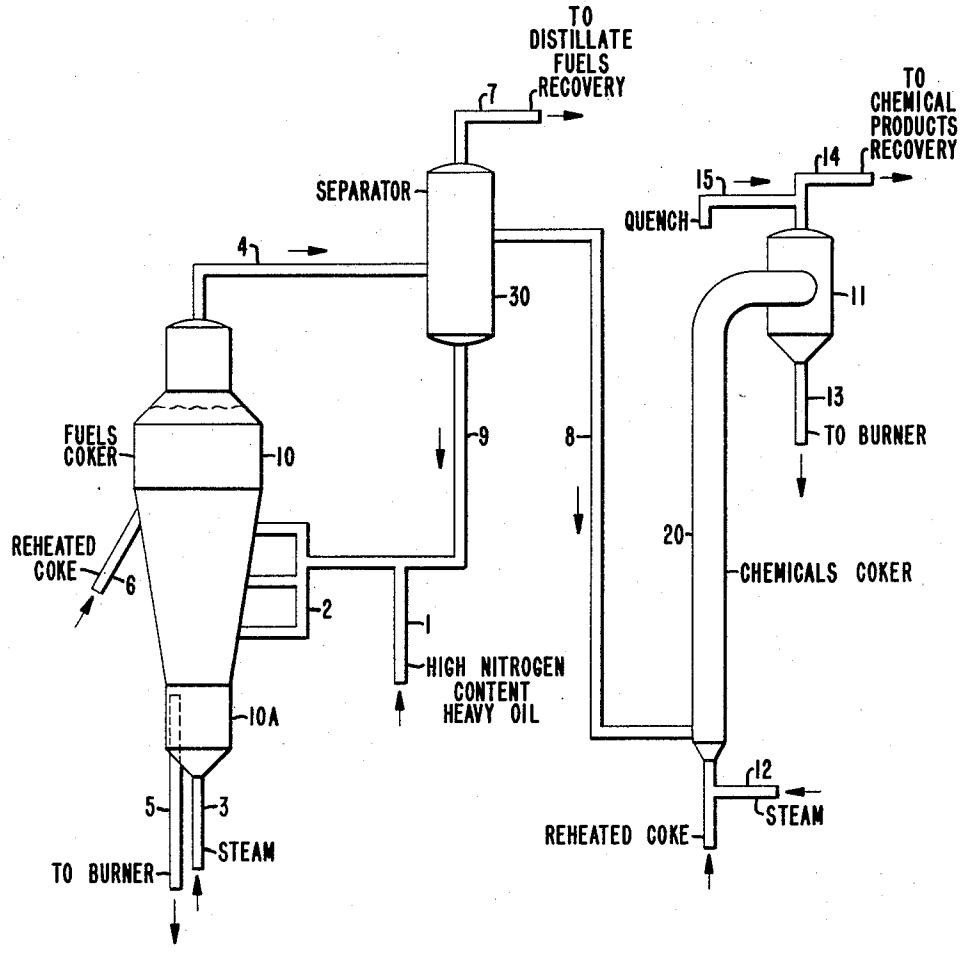
Sept. 29, 1959 J. F. MOSER, JR 2,906,689

TWO-STAGE RESIDUUM COKING CONVERSION PROCESS

Filed March 18, 1955



JOHN F. MOSER, JR. INVENTOR

BY L. Chasan ATTORNEY

United States Patent Office 2,906,689 Patented Sept. 29, 1959

2,906,689

TWO-STAGE RESIDUUM COKING CONVERSION PROCESS

John Frederick Moser, Jr., Baton Rouge, La., assignor to Esso Research and Engineering Company, a corporation of Delaware

Application March 18, 1955, Serial No. 495,179

3 Claims. (Cl. 208—53)

The present invention relates to the art of residuum conversion. More particularly it pertains to a fluidized solids process for upgrading heavy oils, particularly oils of high nitrogen content, to hydrocarbon distillates suitable for use as fuels, and to hydrocarbons suitable for use as chemicals or chemical intermediates.

In its more specific aspects, this invention proposes a two-stage combination process for converting high nitrogen content heavy oils such as reduced crudes, shale oils, tars, and asphalts, into lighter and more valuable products.

The present process comprises the steps of converting a heavy oil in a fluidized solids fuels coking zone operating at a temperature in the range of 900° to 1100° F. to vapors and coke which is deposited on the fluidized solids. The vapors so produced are then separated to obtain light distillate products and a distillate gas oil boiling in a range within the limits of 700° to 1000° F. This gas oil is then converted in a transfer line chemicals coking zone at a temperature in the range of 1200° to 1600° F. to light unsaturates desirable as chemicals or chemical intermediates. The heavy ends of the fuels coker effluent are recycled substantially to extinction. A common heating system may be used to supply the necessary heat for the pyrolysis in the form of high temperature solids to both the fuels and the chemicals coking zones.

This invention has particular applicability to the treatment of heavy oils which upon being pyrolytically upgraded yield a gas oil which, by reason of its high nitrogen content, ash content, or aromaticity, is decidedly unsuitable as a catalytic cracking feed stock. As examples of typical heavy oil feed stocks, there may be mentioned California residua such as Zaca, Santa Maria and Los Angeles Basin, shale oils and coal tars, etc.

A principal object of this invention is to devise a combination fuels and chemical coking process that can economically process such heavy oil feeds that normally produce gas oils of unsatisfactory or poor catalytic cracking quality. Another object of this invention is to develop a fluid solids process that will satisfactorily upgrade heavy oils such as reduced crudes, a major portion of which boils above 900° F., characterized by API gravities of −10° to 20°, Conradson carbons of 5 to 50 wt. percent, and nitrogen contents of over 0.6 wt. percent.

The following description of the attached drawing will serve to make this invention more clear. The attached drawing depicts schematically a preferred embodiment of the two-stage combination process of this invention. The major items of equipment shown are a fluid coking reactor **10** operated primarily to produce lighter distillate products from heavy oils, and a transfer line reactor **20** operated to produce primarily light hydrocarbon unsaturates. Adjunctive equipment such as cyclonic separators, fractionation zones and a solids heating zone or zones also form elements of the process.

The heavy oil to be upgraded which may be suitably preheated is introduced into the process via line **1** and is introduced in the fuels coker **10** via manifold injection system **2**. The fuels coker contains a fluid bed of substantially catalytically inert solids, preferably coke particles produced by the process, having a particle size in the range of 0 to 1000 microns and at a coking temperature in the range of 900° to 1100° F., the fluidity of the bed being accomplished by injection of a fluidizing gas, e.g., steam, into the vessel via line **3** in amounts sufficient to secure fluidizing gas velocities in the range of 0.1 to 5 ft./sec., all of which is conventional and known in the art.

Upon contact with the hot solids, the heavy oil is partially vaporized and partially coked, the vapors being withdrawn overhead via line **4** after having entrained solids removed. Relatively cool solids with fresh deposits of coke are removed from the fuels coker via line **5** after being stripped of occluded hydrocarbons in stripping zone **10***a* and are circulated to a heating zone, e.g., a fluid burner, wherein the solids are reheated by partial combustion. Reheated solids are returned to the fuels coker via line **6** at a temperature 100° to 300° F. above the coking temperature. Solid/oil circulation ratios are maintained within the range of 5/1 to 30/1 wt./wt.

A fluid bed reactor is preferred for carrying out this fuels coking reaction as a relatively long time must be allowed for the coking reaction. Average solids holding times in the order of 4 to 30 minutes are maintained in the fuels coker.

The vaporous effluent from the fuels coker in line **4** is passed to separation zone, e.g., a scrubber-fractionator **30**, wherein at least a light distillate fraction is recovered and removed as product via line **7** and a gas oil fraction boiling above about 700° F. is separated and removed via line **8**. The heavy high boiling ends, boiling above about 1000° to 1150° F., that have approximately the same coking and vaporization characteristics as the fresh feed, are recycled to the fuels coker via line **9** substantially to extinction.

The initial boiling point of gas oil fraction in line **8** is adjusted so that it will contain all, or substantially all, of the deleterious compounds such as nitrogen that would adversely affect the quality of the products removed by line **7**. It has previously been suggested to recycle this gas oil which is not amenable to catalytic cracking to the fuels coker in order to reduce it completely to lighter distillates. As conversion of this material must take place in the vapor phase because of its low boiling range, such recycle operation is not attractive. Because the coking temperature in the fuels coker is relatively low, high conversions of the gas oil which is refractory are difficult to obtain. This results, then, in excessive recycle rates. This difficulty cannot economically be circumvented by increasing the coking temperature in the fuels coker because this results in an excessive thermal degradation and loss of the light distillate products.

This invention proposes that this gas oil material be converted to useful chemical raw materials. This is done by injecting it into a transfer line chemicals coker **20**. Thus the former onerous recycle operation to reduce this gas oil is obviated.

The initial boiling point of the gas oil fraction can also

be adjusted, if it be desired, to balance the amount of the fresh feed converted to distillate fuels and to chemicals. In normal operations, it is preferred to maintain 430° F. conversions [1] in the fuels coker in the range of 30 to 60 vol. percent, and to maintain C_3– conversions [2] in the chemicals coker in the range of 50 to 80 wt. percent. In this manner approximately 40 to 60 vol. percent of the fresh feed will be upgraded to light distillates, and the remainder, excluding coke, will be converted to chemical raw materials including light unsaturates such as ethylene, propylene, butenes and butadienes and aromatic tars.

The gas oil fraction in line **8** introduced into a transfer line chemicals coker **20** is admixed with freshly heated solids, preferably coke particles produced by the process having a size in the range of 0 to 1000 microns. The solids are at temperatures in a range of 1300° to 1800° F., and are admixed with the gas oil in amounts in the range of 2 to 20 lbs. per lb. of gas oil sufficient to obtain a reaction temperature in the range of 1200° to 1600° F.

The transfer line reactor comprises a narrowly confined vertically disposed elongated conduit, suitably lined with a refractory material, and terminates in a cyclonic separator **11**. The length of the reactor is such that reaction times before quenching in the order of 0.1 to 3 sec. are achieved. A conveying gas, e.g., steam, light hydrocarbon gases, nitrogen or flue gases, is admitted to the base of the reactor via line **12** in amounts sufficient to achieve solids velocities in the transfer line reactor above 10 ft./sec., e.g., 60 ft./sec. The density of suspension in the transfer line reactor will range from 1 to 20 lbs./cu. ft.

The entrained solids are separated from the conversion products in separator **11** and are transferred by line **13** to a heating zone to be reheated. The conversion products removed from the cyclone by line **14** may be met with a quench supplied by line **15** to be cooled to a temperature below about 900° F. whereby further thermal reaction is arrested. This quench may comprise liquid, e.g., water, or cool oils, solids, e.g., cool coke particles, or gases, e.g., cool light hydrocarbons or steam. The conversion products are then subjected to further processing (not illustrated) to recover the desired chemicals. This further processing may include by way of illustration, fractionation, sorption, crystallization, extraction, extractive or azeotropic distillation and polymerization. The higher boiling material recovered from the chemicals coker effluent may conveniently be recycled to the fuels coker and/or the chemicals coker depending upon the boiling range of the material or may be marketed directly as specialty tars.

Heat for the process may be generated by burning a portion of the coke produced by the cracking reactions. In cases where the value of the coke is greater than other extraneous liquid or gaseous fuels the latter may be burnt to supply part or all of the required heat to the circulating coke particles. The contact solids used in the fuels and chemicals cokers may traverse essentially separate circuits or a common heating zone may be used. Fluid gravitating or moving bed burners or transfer line burners may be used to accomplish the heating of the solids. Also other direct or indirect heat exchange means may be used such as systems wherein heavy heat-carrying inert particles, e.g., "shot," are mixed with the contact solids.

Example

A heavy oil feed may comprise a California residuum having the following inspections: 4.3° API gravity, 908° F. initial boiling point, 24.2 wt. percent Conradson carbon, 1.3 wt. percent sulfur, 0.08 wt. percent ash at 1742° F., 1.2 wt. percent nitrogen, and a viscosity at 275° F. of 317 SSF. The feed, preheated to a temperature of 500° F., is injected into the fuels coker maintained at a pressure of 6 p.s.i.g. having a fluid bed of coke particles of a size range of 50 to 1000 microns (250 microns median particle size) and a temperature fo 950° F. A bed density of 38 lbs./ft.^{3} is maintained at an average superficial fluidizing gas velocity of about 1.5 ft./sec. (requiring a fluidizing steam rate of 12 wt. percent on fresh feed). Reheated coke particles are supplied to the fuels coker at a temperature of 1125° F. and at circulation rate of 10 lbs./lb. of fresh feed. Under these conditions, a 430° F. conversion of 48.5 vol. percent is obtained. The fuels coker effluent is separated to obtain a gas oil boiling in a range of 700° to 1000° F., amounting to 25 vol. percent on fresh feed, and heavy ends boiling above 1000° F., amounting to 15 vol. percent on fresh feed. The heavy ends are recycled to extinction to the fuels coker.

The 700° to 1000° F. gas oil is admixed with 6 lbs./lb. of gas oil of coke particles at an initial temperature of 1600° F. 60 wt. percent on gas oil feed of steam at a temperature of 1000° F. is admixed with this suspension, and the resulting mixture is passed through the transfer line reactor at a velocity of 30 ft./sec., a density of 3 lbs./ft.^{3}, an average temperature of 1300° F., and an outlet pressure of 6 p.s.i. Reaction time before quenching is maintained at 1 sec. sufficient to secure a C_3– conversion of the gas oil of 40 wt. percent.

Approximately 26.6 wt. percent of the fresh heavy oil feed will be converted to coke in the fuels coker, and less than 1 wt. percent of the gas oil will be converted to coke in the chemicals coker. In all, approximately 27 wt. percent of the fresh feed to the process will be degraded to coke, of which 10 wt. percent on feed will be burnt to supply heat to the process, and the remainder is removed as product.

Under these conditions, the following product yields are obtained from the California residuum based on fresh feed:

Hydrogen	wt. percent	0.2
Methane	do	5.3
Ethane	do	3.0
Ethylene	do	4.1
Propane	do	2.0
Propylene	do	4.7
475° F. to 650° F. aromatic tar	vol. percent	4
C_5 to 430° F. naphtha	do	25.0
430° F. to 700° F. gas oil	do	26.5

Having described this invention, and a preferred embodiment, what is sought to be protected by Letters Patent is succinctly set forth in the following claims.

What is claimed is:

1. A two-stage combination fuels and chemicals coking process for converting heavy hydrocarbon oils boiling mostly above 900° F., and which produce gas oils of unsatisfactory catalytic cracking quality upon coking, which comprises coking a heavy oil boiling mostly above 900° F. in a dense fluidized solids fuels coking zone containing finely divided coke particles at a temperature in the range of about 900° F. to 1100° F., to produce vaporous conversion products and coke at a 430° F.- conversion in the range of 30 to 60 vol. percent and recovering from said vaporous conversion products light distillate hydrocarbon products boiling below about 700° F., heavy ends boiling above about 1000° F. and a gas oil fraction boiling in a range of about 700° F. to 1000° F., then cracking said gas oil fraction by contact with finely divided coke at a higher temperature than said first stage and in the range of about 1200° F. to 1600° F. for a relatively short time in a separate upflow vertically arranged chemicals transfer line coking zone to produce normally gaseous unsaturated hydrocarbons suitable as chemicals and chemical intermediates at a

[1] 430° F. conversion is defined as 100 vol. percent of fresh feed to the fuels coker less vol. percent of products from fuels coker boiling above 430° F., excluding coke.

[2] C_3– conversion is defined as 100 vol. percent of gas oil feed to the chemicals coker less vol. percent of products having more than 3 carbon atoms, excluding coke.

C_3– conversion in the range of 50 to 80 wt. percent and circulating said finely divided coke from each of said coking zones to a heating zone wherein the particles are reheated by partial combustion and back to maintain the respective reaction temperatures in said zones.

2. The process of claim 1 wherein said heavy hydrocarbon oil is typified by inspections in the following ranges: −10° to 20° API gravity, 5 to 50 wt. percent Conradson carbon and a nitrogen content over 0.6 wt. percent.

3. The process of claim 1 wherein said heavy ends

boiling above about 1000° F. are recycled to said fuels coking zone substantially to extinction.

References Cited in the file of this patent

UNITED STATES PATENTS

2,636,844	Kimberlin et al.	Apr. 28, 1953
2,690,990	Adams et al.	Oct. 5, 1954
2,731,508	Jahnig et al.	Jan. 17, 1956
2,768,127	Kimberlin et al.	Oct. 23, 1956
2,813,916	Boston	Nov. 19, 1957