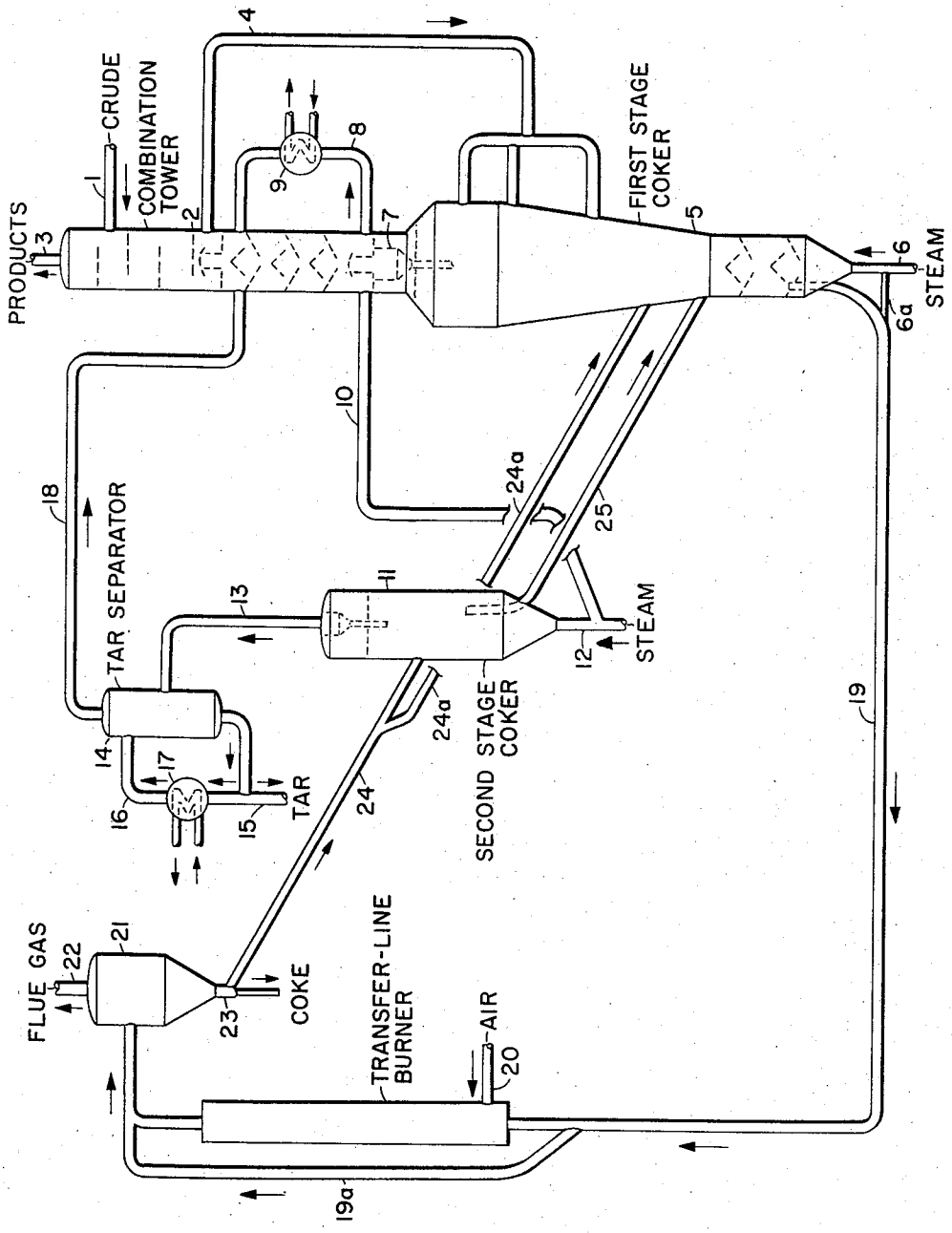
March 24, 1959 J. W. BROWN 2,879,221

HYDROCARBON OIL CONVERSION PROCESS

Filed July 15, 1954



JAMES W. BROWN *INVENTOR.*

BY L. Chasan

ATTORNEY

United States Patent Office 2,879,221 Patented Mar. 24, 1959

2,879,221

HYDROCARBON OIL CONVERSION PROCESS

James W. Brown, Mountainside, N.J., assignor to Esso Research and Engineering Company, a corporation of Delaware

Application July 15, 1954, Serial No. 443,473

4 Claims. (Cl. 208—53)

This invention relates to the art of upgrading hydrocarbon oils by pyrolysis. In its more particular aspects, this invention is concerned with a two-step fluidized solids process for coking low value, high-boiling petroleum residual oils, particularly oils containing a predominate proportion of refractory hydrocarbon constituents that upon thermal cracking degrade mostly to light gases and carbonaceous residue. The present invention is particularly suited to the processing of highly aromatic crudes, distillate and residual fractions therefrom, or mixtures thereof.

In a conventional fluid coking process wherein a heavy residual oil is upgraded by contacting fluidized solids maintained at a temperature in the range of about 850° to 1000° F., the end point of the distillate fractions obtained from the process is usually about 1050° to 1200° F. and the remaining heavy ends are normally recycled substantially to extinction. The portion of the products boiling above about 700° F. are usually subjected to catalytic cracking to obtain further quantities of naphthas and light and middle distillates.

Many heavy oils, upon being coked, yield high boiling distillates that contain a high percentage of ash, nitrogen, aromatic, or carbon-forming constituents. Such distillates are, therefore, unattractive as feed stocks to catalytic cracking because of catalytic coke production and catalyst contamination. To secure a better catalytic cracking feed stock, it is possible, in some instances, to recycle more of the heavy gas oil, such as 700° F.+ products, to the coking zone, but recycle rates become uneconomically high. Also, the product values from recycle operations are usually unattractive, because the yield and quality of the gasoline and heating oil produced are inferior to those secured through catalytic cracking.

Further, it is often desirable or necessary to make final products, by fluid coking, boiling entirely below about 700° F., particularly when the coker feed stock is highly aromatic or high in nitrogen content such that the 700° F. and heavier coker gas oil is of exceptionally low value as feed for catalytic cracking. Thus, it may be desired to conduct the coking operation to obtain materials up to light gas oils, with the gas oils being sold as heating oils.

In cases where catalytic cracking capacity is not available, it may be desired to secure light and middle distillates boiling below about 700° F. to meet market demands by coking a heavy oil with recycle to extinction of the coker products boiling above 700° F.

Many oils are partly composed, in predominate proportions, of high boiling exceptionally refractory constituents, usually condensed ring aromatic-type hydrocarbons. These ring compounds may be joined by sulfur, nitrogen and oxygen linkages as well as by carbon-carbon bonds. Coking temperatures in the nature of 1200° to 1300° F. are necessary to secure reasonable conversions, e.g., 50%, of such refractory materials and the conversion products are mostly coke and gas. If

recycle operation at conventional temperatures is practiced in a process coking oils containing such constituents, high conversion per pass is unattainable and these refractory constituents tend to pass through the coking zone substantially unaltered thereby creating exceptionally high recycle rates. If higher temperatures are used to obtain severe cracking and high conversions of the oil, including its refractory constituents, secondary vapor phase cracking becomes pronounced and product distributions and yield become extremely poor. At high temperatures, a large portion of the oil is converted to light gases at the expense of the desired distillate fractions.

As these highly refractory constituents form mostly light gases and coke when thermally cracked, there is little advantage obtained by cracking them. It is, therefore, economically desirable to thermally treat an oil at minimum cracking severities, consistent with coverting all amenable compounds to lighter distillates while avoiding severities that transform such refractory constituents.

Accordingly, it is an object of the present invention to convert hydrocarbon oils, particularly heavy residual oils, containing predominate proportions of refractory constituents and/or catalyst fouling constituents, to maximum yields of light and middle distillates. Another object is to devise a multi-stage fluidized solids coking process that eliminates the necessity of recycle operation, to obtain high yields from certain petroleum oils. A more particular object is to present to the art a two-stage coking process for pyrolytically upgrading heavy petroleum residua boiling above a temperature in the range of 500° to 1000° F., the residua being characterized by a low API gravity, e.g., —10° to 20°, high Conradson carbon, e.g., 5 to 50 wt. percent, a high viscosity, e.g., 5 to 500 SSF at 335° F., and high ash content. Residua of this type may contain up to 4 wt. percent nitrogen, up to 8 wt. percent sulfur, and up to 300 parts per million each of nickel and vanadium. It is also an object of the present invention to utilize the vapors produced by the coking process to supply heat and diluent for the initial separation of a whole crude and to preheat the feed to the coking process.

These and other objects and advantages will become readily apparent as this description proceeds and the attached drawing, forming a part of this specification, is discussed in detail. The attached drawing diagrammatically depicts a two-stage fluidized solids coking process with a combination fractionation tower, designed to achieve the objects of this invention.

Generally, the objects of this invention are attained by coking an oil of the type described by contact with particulate coke in a fluidized state in a coking zone operating at temperatures and conversions designed to secure maximum yields of naphthas and heating oils while avoiding undue thermal degradation of the products, i.e., temperatures in the range of 850 to 1000° F., and 700° F.+ conversions in the range of 30 to 70%. 700° F.+ conversion is defined as: 100 vol. percent feed to coker minus products boiling below 700° F. Material boiling above the heating oil endpoint is then separated from the effluent from the coker and treated in a second fluid bed coking zone at higher temperatures and severities designed to maximize the yields of light and middle distillates, and to leave as residue only refractory, gas and coke producing materials, i.e., temperatures in the range of 1000° to 1200° F., 700° F.+ conversions in the range of 50 to 90%, or with vapor cracking times of 10 to 35 seconds. The heavy ends remaining after the second stage are segregated and removed from the process as product.

It will be apparent that by operating the first and second coking zones at lesser severities, some material susceptible to further conversions will remain in the residue or tars from the second stage and, therefore, that further

coking stages may be used. It has been found, however, that optimum yields of liquid distillates can be obtained from practically all types of oils by using only two coking stages. The selectivity of a coking operation to naphtha and heating oil does not drop off in the second stage as cracking severity is increased, as one might expect. Consequently, the use of more than two coking stages usually will be uneconomical and will result in partially negligible increases in product yields and distributions.

To attempt to secure the same ultimate conversion of an oil by a single coking zone, however, necessarily requires the use of higher temperatures and/or recycle rates and results in lower yields and unfavorable product distributions and qualities. Further, in a single stage recycle process, coking a highly aromatic oil, if a sizeable net withdrawal of 700° F.+ aromatics is made, a substantial loss of 700° F.+ product from the first pass occurs, this material being mixed with the 700° F.+ aromatics from subsequent passes.

The advantage of the present two-stage process is shown by the following example comparing the yields obtainable from single and multiple stage coking processes when processing a 700° F.+ Coleville residuum to obtain 84.5% ultimate 700° F.+ conversions.

Products, Vol. Percent based on feed	Single Stage Coking at 1,000° F. with Recycle	Two-Stage Coking at 950° F. and 1,050° F.
C_4–430° F.	30.4	31.2
430°–700° F.	24.4	28.1
	Three-Stage Coking at 950° F., 950° F., and 1,050° F.	Four-Stage Coking at 950° F., 950° F., 1,050° F. and 1,050° F.
C_5–430° F.	30.0	29.5
430°–700° F.	29.5	30.0

It is to be appreciated that not only is the yield of naphtha from 3 to 4-stage cokers less, but it is of lesser octane.

This invention also involves the feature of using a single heating zone for the two-stage process, although separate heating zones may be used for each coking stage, if desired. In the preferred embodiment of the invention, a transfer line burner is used to heat the particulate contact solid. However, a fluid bed burner, gravitating bed burner, or shot heating system can well be used. Further, liquid gaseous or solid fuels, other than the coke produced by the process, may be used to heat the heat-carrying solids.

Although coke produced by the process having a particle size in the range of about 0 to 1000 microns is the preferred heat-carrying contact solid, other finely divided solids such as sand, spent catalyst, refractory particles, etc., can also be used. The use of coke as an example is intended to be non-limiting.

At coking temperatures in the range of 850° to 1100° F., fluid bed coking vessels are preferred in order that there be sufficient time for the cracking to occur. However, in many applications of this invention, transfer line cokers may be used for either of the coking zones, particularly for the second zone. In a transfer line coker, the oil being upgraded is conveyed through a narrowly confined, elongated path in admixture with the heat-carrying solids at velocities above 10 feet/sec., e.g., 60 feet/sec., as is known by the art.

For convenience, the operating conditions applicable to the following example are summarized in Table I. Referring now to the drawing, the feed to the process is introduced by line **1** into a combination tower **2**. The crude oil is separated into products boiling below about 700° F., which are removed by line **3**, along with products from the coking reaction. This particular arrangement is advantageous in that the coker effluent supplies the heat necessary for the distillation and preheats the feed to the coker. The remainder of the oil is withdrawn from the middle of the tower by line **4** and injected into the coking vessel **5** at a plurality of points.

There is maintained in the coking vessel a fluidized bed of particulate coke at a relatively low coking temperature so as to avoid undue degradation of the initial conversion products. Steam is supplied to the coking vessel by line **6** and serves first to strip the particulate coke of adhering liquid hydrocarbons before it is circulated to the burner, and then serves to fluidize the main coking bed.

It will be clear to those skilled in the art that although steam is used in this example as the fluidized medium other media may be used. Thus, inert gases, light hydrocarbon gases, etc. can be used to maintain the fluidity of the beds.

The injected oil, upon contact with the high temperature coke particles, undergoes pyrolysis, evolving lighter hydrocarbon vapors and depositing carbonaceous residue on the coke. The vapors conversion products pass upwardly through the coker and thence through cyclone **7**, wherein entrained solids are removed. The vapors continue upwardly through the combination tower **2**. In the lower portion of the tower heavy, aromatic-containing ends are separated from the vapors. After this, the vapors preheat the feed to the coker and then are separated with the crude. A pump-around system is used to regulate the temperature of the tower. A portion of the heavy ends separated from the coker effluent in the lower part of the tower is withdrawn by line **8**, cooled by means of heat exchanger **9** and then reintroduced into the tower to scrub the ascending vapors. The fresh feed to the unit, in line **1**, may conveniently be used as a heat exchange medium in heat exchanger **9**. The net heavy ends from the coker effluent boiling above the end boiling point of the products, e.g., above 700° F., are transferred to a second stage coking zone **11** by line **10**.

The second stage coker also contains a fluid bed of coke. As it operates at higher temperatures, very little solids hold-up is required for operability of the fluid bed. Steam is admitted to the base of the second stage coker by line **12** to fluidize the solids therein. The exact conditions in the second coking stage are selected so as to maximize the yield of naphtha plus heating oil, while leaving as residua only refractory constituents not amenable to thermal cracking. Thus, the second coking stage operates at temperatures in the range of 1000° to 1200° F., preferably 1000° to 1075° F. At these temperatures, the second coking stage will produce a relatively high octane naphtha.

After having entrained solids removed, the conversion products are transferred from the second stage to a tar separator **14** via line **13**. The tar separator is used to remove the high boiling ends that have very little, if any, value as thermal cracking feed stock. The heavy tar is removed from the separator by line **15** and a portion of it is recycled by line **16**, after being cooled in the heat exchanger **17**, to serve as a quench oil. The lower boiling portion of the vapors is transferred to the combination tower **1** by line **18** to be separated therein.

In some applications of this invention, it may be desired to keep the virgin distillates separate from the thermally cracked distillates. If so, this combination tower may be dispensed with and separate products recovery system used. In such a case, indirect heat exchange means can be used to recover heat from a coker effluent.

To maintain the coking temperatures, stripped coke is removed from first stage coker **5** by line **19** and transferred to a transfer line burner. Steam is admitted by line **6a** to line **19** to convey the coke. A free oxygen-containing gas, e.g., air, is admitted to the burner by line **20**. The resulting mixture flows through the burner undergoing combustion. It is desirable to transfer some

of the cool coke to the outlet of the burner by line 19*a*. This allows the burner to operate at a higher temperature. This cooler coke serves to quench the burner effluent and minimizes the loss of heat in the flue gas besides simplifying cyclone construction. The heated coke particles at a temperature 100° to 300° F. above the highest coking temperature are then separated from the flue gases in cyclone system **21**, the flue gases being vented to the atmosphere by line **22**. The excess of coke, beyond that required to supply heat, is removed from the process by line **23**. The remainder of the high temperature coke is transferred by lines **24** and **24***a* to the second and first stage cokers. The coke in the coker **11**, being at a higher temperature, is transferred by line **25** to the first stage coker to supply heat thereto. Of course, to maintain heat balances, all of the heated coke from cyclone system **21** may be conveyed directly to coker **11**. Also, coke may be transferred from the second stage coker directly to the burner.

Table I summarizes the pertinent range of operating conditions applicable to the two-stage coking process of this invention as depicted in the drawing and presents a specific example of operating conditions. Table II illustrates the products obtainable from this process when operating in accordance with the example of Table I.

TABLE I

Operating conditions

	Range	Example
First Stage Fluid Coker:		
Temperature, ° F.	850 to 1,000	950
Pressure, p.s.i.g.	0 to 50	10
Fresh Oil Injection Rate, lbs./hr./lb. coke in coker	0.3 to 3.0	1.2
Fluidizing steam, lbs./lb. oil injected	0.03 to 0.20	0.1
Coke circulated to coker, lbs./lb. fresh oil	5 to 15	7.3
700° F.+ Conversion, vol. percent	30 to 70	45
Second Stage Fluid Coker:		
Temperature, ° F.	1,000 to 1,200	1,050
Pressure, p.s.i.g.	0 to 50	10
Oil Injection Rate, lbs./hr./lb. coke in coker	0.3 to 5.0	2.0
Fluidizing Steam, lbs./lb. oil injected	0 to 0.1	0
Coke circulated from burner, lbs./lb. oil injected	5 to 15	8.0
700° F.+ Conversion, vol. percent	50 to 90	72
Transfer Line Burner:		
Temperature of coke from cyclone, ° F.	1,100 to 1,500	1,250
Burner outlet temperature, ° F.	1,200 to 1,800	1,500
Pressure, p.s.i.g. @ top	0 to 50	2
Throughput,[1] Tons coke/sq. ft./hr.	5 to 15	10.8
Air Rate, s.c.f./bbl. total oil feed	1.0 to 3.0	1.85
Percent of heated coke circulated directly to first stage	0 to 80	40
Initial Boiling Point of first stage coker feed, ° F.	500 to 1,100	700
Initial Boiling Point of second stage coker feed, ° F.	500 to 900	700
Initial Boiling Point of tar product, ° F.	500 to 800	700

[1] Not including quench coke circulated to burner outlet.

TABLE II

Feed: Coleville Crude—
- Inspections:
  - 13.8° API gravity
  - 2.9% sulfur
  - 7.4% Conradson carbon residue
  - 3080 SSU @ 100° F.
  - 72% 700° F.+residuum on crude
  - 49% 1000° F.+residuum on crude

Total products: Percent based on crude—

C_3 and lighter	9.3 wt. percent.
C_4	3.2 vol. percent.
C_5—330° F. (88 clear research octane)	18.4 vol. percent.
330°–430° F. (85 clear research octane)	9.5 vol. percent.
430° F.–700° F.	37.4 vol. percent.
700° F.+tar	16.1 vol. percent.
Gross Coke	14.1 wt. percent.
10# R.V.P. Gasoline (89 clear research octane and including polymerization gasoline)	32.2 vol. percent.

Internal flows:

700° F.+residua to first-stage coker	72 vol. percent on crude.
700° F.+ends to second-stage coker	40 vol. percent on crude.

It is not necessary to use a separate vessel for the second coking stage so long as the refractory tar can be separately recovered from the second stage effluent without being mixed in with the feed to the second stage. Thus, a second stage coking zone can be located in the same vessel as the first stage, the two having separated by a barrier or baffle and separate gas outlets being used for each zone.

The process of this invention should not be confused with simple recycle to a higher severity or higher temperature zone in a fluid coker which allows commingling of the vapors from each zone. The segregation of the refractor product is essential in reducing recycle rates and in improving over-all yields. To illustrate, simple recycle to a hot zone in a coking reactor results in mixing the heavy ends containing the refractory constituents with the feed to the unit. Therefore, such operations result in having to feed, say about 167 bbls. of oil into the coker/100 bbls. of fresh feed compared to 155 bbls. in the two-stage coker example. Furthermore, it usually is necessary in such a system to bleed some of the recycle to prevent build-up of refractory and ash-forming constituents. This bleed may contain as much as 60% of readily crackable materials.

As another illustration, if the feed to a single stage coker is directly contacted with the coker vaporous products, so as to be preheated, then the total feed to the coker is even higher than that of the previous examples, e.g., high as 200 bbls./100 bbl. of fresh food. If a purge is made, approximately 50% of the purge will be fresh feed. If the temperatures or severity of the cracking in this illustration be increased to decrease the recycle rate, product distribution and yields become extremely poor.

It can be appreciated then that this invention processes oils containing refractory and ash-forming constituents in such a manner so as to obtain optimum product yields of product having a low end boiling point, while avoiding the necessity of recycle operation.

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

What is claimed is:

1. A method of processing a heavy, aromatic petroleum oil, comprising injecting the petroleum oil containing high boiling refractory constituents non-vaporizable without thermal degradation into a first fluidized coking zone containing a dense turbulent bed of finely divided coke maintained at a coking temperature in the range of 850° to 1000° F. whereby said oil is pyrolytically upgraded, depositing carbonaceous residue on said finely divided coke and evolving considerable quantities of relatively lighter hydrocarbon vapors, stripping coke of adhering hydrocarbons before circulating said coke from said coking zone to a heating zone, separating from the effluent from said coking zone products boiling below an end boiling point in the range of 500° to 900° F., injecting the aromatic-containing remainder of said effluent boiling above said end boiling point into a second fluidized coking zone containing a dense turbulent bed particulate coke maintained at a higher coking temperature in the range of 1000° to 1200° F. whereby said remainder is pyrolytically upgraded, depositing carbonaceous residue on said particulate coke and evolving further quantities of relatively lighter hydrocarbon vapors,

separating from the vapors issuing from said second coking zone further amounts of products boiling below said end boiling point and a heavy tar residue, said residue being composed primarily of said high boiling refractory constituents, withdrawing said separated heavy tar residue from said second coking zone without subjecting it to further coking reactions, said finely-divided coke being heated in a common fluidized heating zone from which the coke is circulated to the second coking zone and thence to the first coking zone and from the first zone back to said heating zone to maintain the coking temperatures.

2. The method of claim 1 wherein a rough separation is made to secure said residue and the vaporous material remaining is commingled with the effluent from the first-mentioned coking and the resulting mixture processed in a common separation zone.

3. The method of claim 2 wherein said separation zone includes a combination fractionation tower integrally connected to said first coking zone for preheating feed to said first-mentioned coking zone and for separating products, wherein a whole crude is introduced into said combination fractionation tower and distillate fractions

are removed from said crude boiling below said end boiling point along with said products, and wherein the remaining fraction of said whole crude is segregated and passed to said first coking zone as said petroleum oil containing high boiling refractory constituents.

4. The process of claim 1 in which the first of said zones operates to obtain a 700° F.+conversion of said oil in the range of 30 to 70%, and the second of said zones operates to obtain a 700° F.+conversion of said higher boiling portion in the range of 50 to 90% when said end boiling point is about 700° F.

References Cited in the file of this patent

UNITED STATES PATENTS

2,018,699	Angell	Oct. 29, 1935
2,102,889	Dubbs	Dec. 21, 1937
2,388,055	Hemminger	Oct. 30, 1945
2,690,990	Adams et al.	Oct. 5, 1954

OTHER REFERENCES

Voorhies et al.: Petroleum Engineer, Reference Annual, 1954, pp. c–3, c–6.