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C. E. JAHNIG ET AL

2,905,617

COMBINATION PROCESS FOR CONVERSION OF HEAVY HYDROCARBONS

Filed March 15, 1956

3 Sheets-Sheet 1

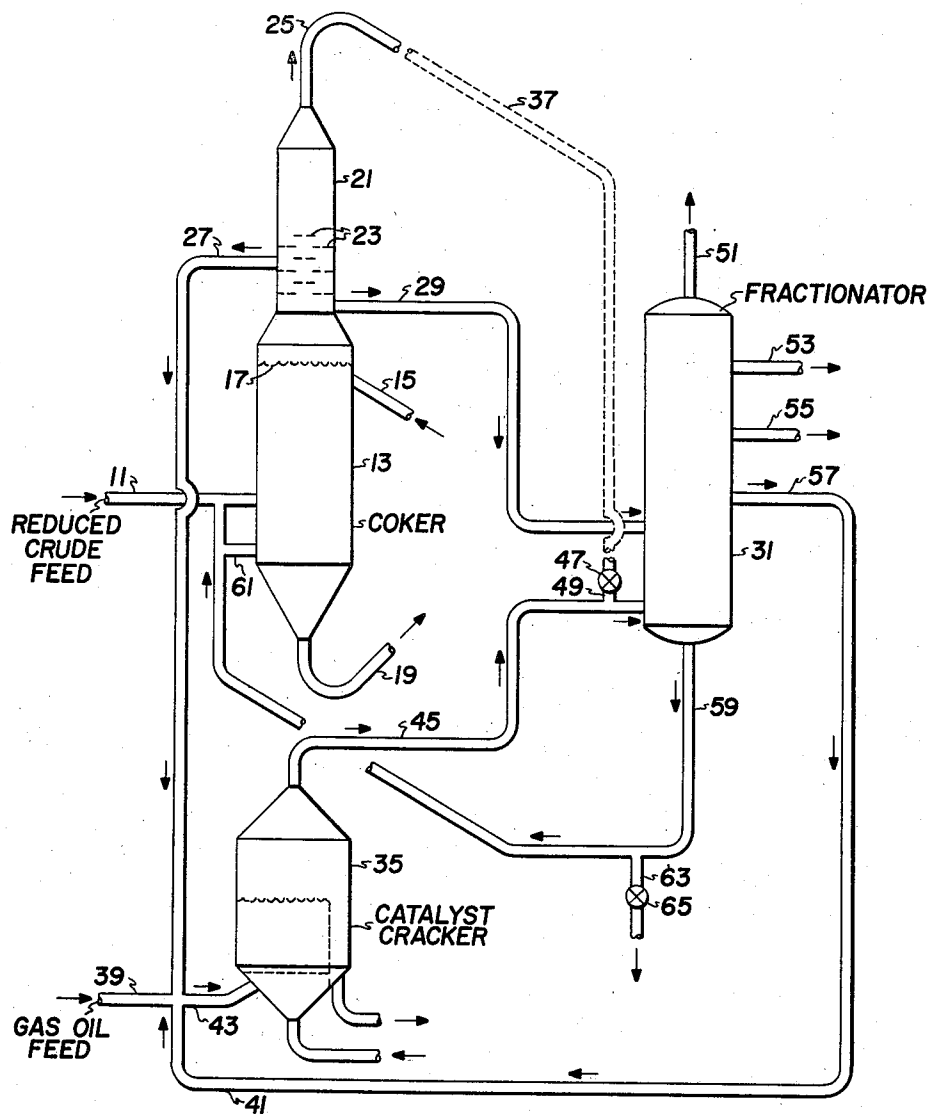


FIG.-1

Charles E. Jahnig
Howard G. Codet

Inventors

By *Small, Dunham & Thomas* Attorneys

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3 Sheets-Sheet 2

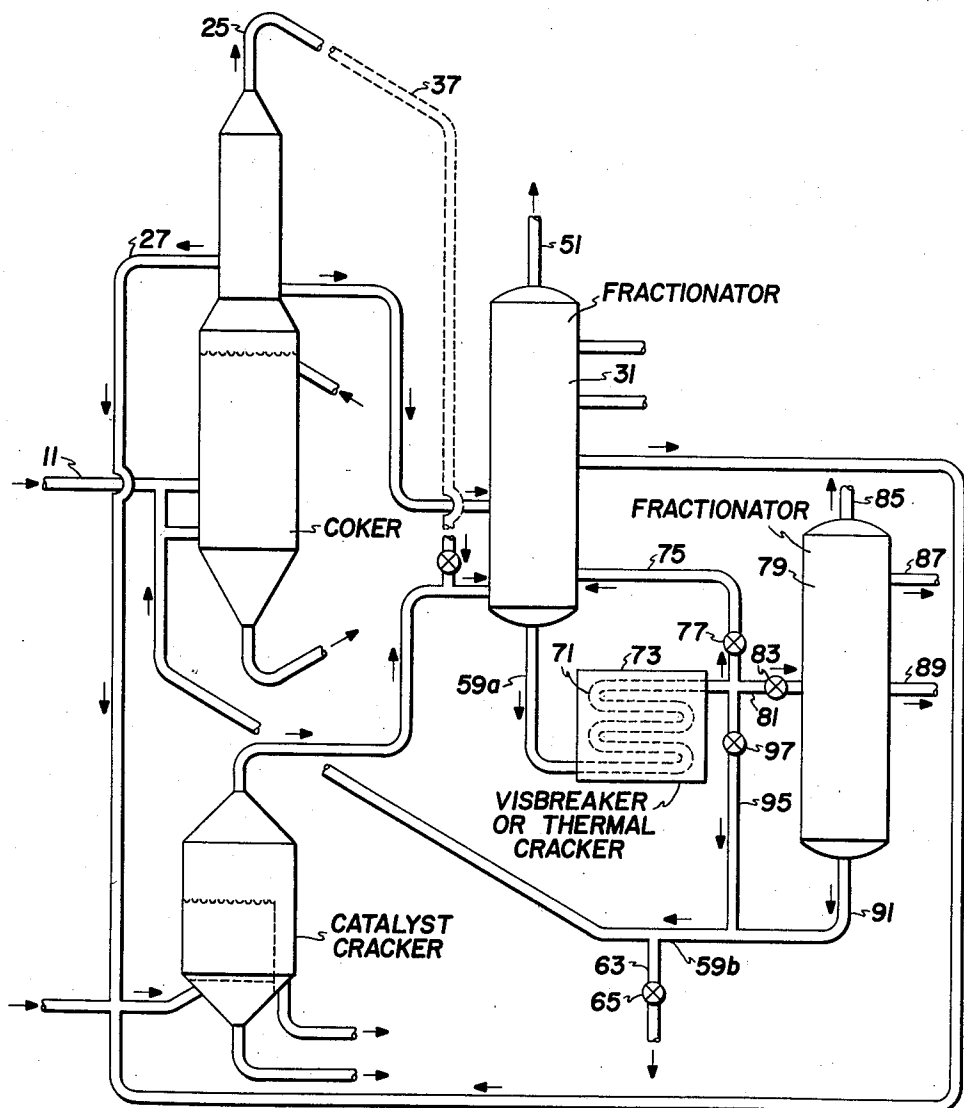


FIG.-2

Charles E. Jahnig
Howard G. Codet

Inventors

By *Small, Dunham & Thomas* Attorneys

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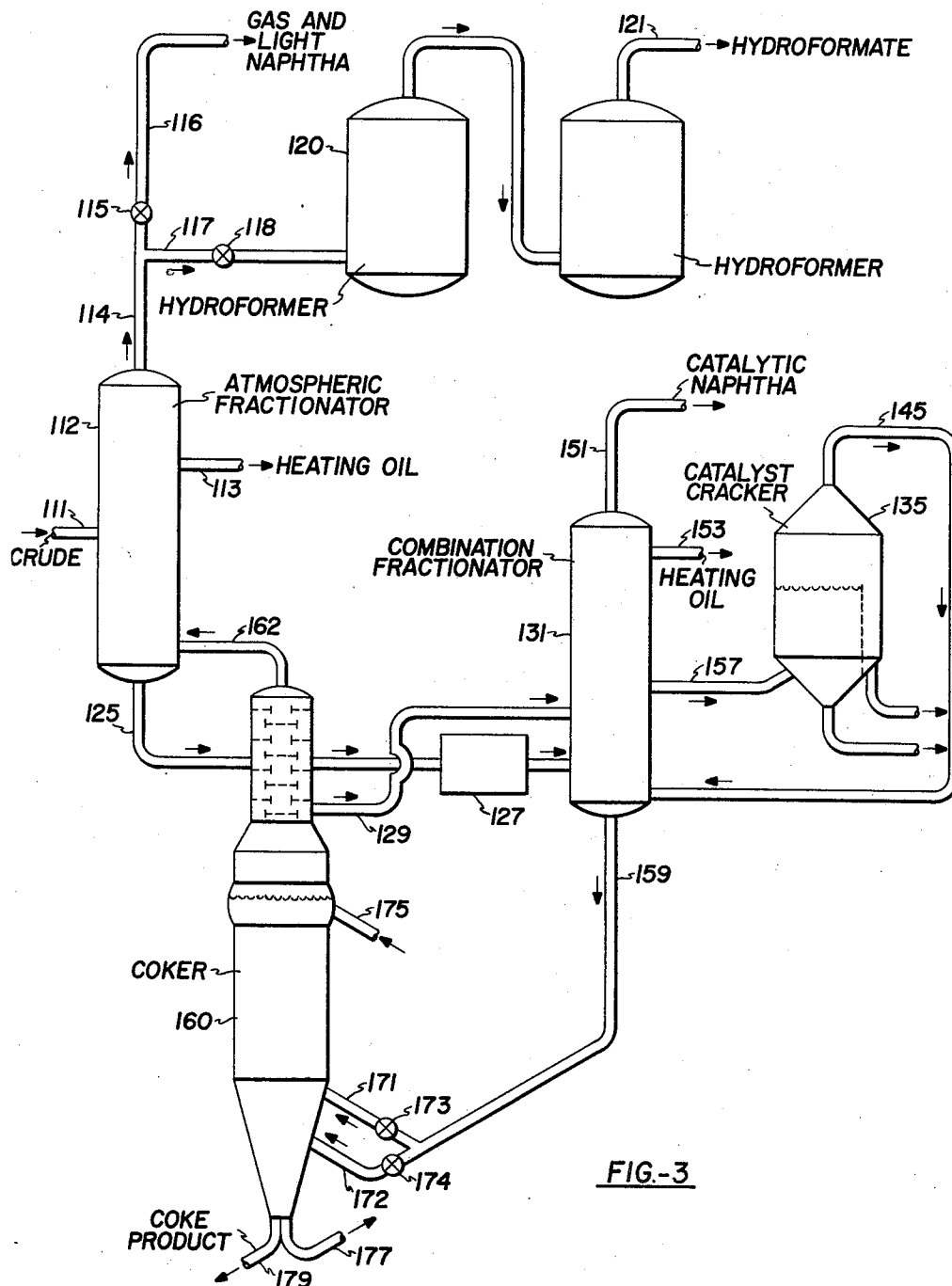


FIG.-3

Charles E. Jahnig
Howard G. Codet

Inventors

By *Small, Shankman & Thomas* Attorneys

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COMBINATION PROCESS FOR CONVERSION OF HEAVY HYDROCARBONS

Charles E. Jahnig, Rumson, and Howard G. Codet, Westfield, N.J., assignors to Esso Research and Engineering Company, a corporation of Delaware

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1 Claim. (Cl. 208—55)

The present invention relates to a combination process and apparatus for the conversion of heavy hydrocarbon oils. The invention pertains particularly to a combination process wherein heavy residual oil is thermally cracked to convert it to more valuable products, a gas oil fraction is catalytically cracked simultaneously, and the vapor heat from catalytic cracking is utilized for fractionating the coker products to obtain cleaner fractions more suitable for catalytic cracking than conventional coker products.

The recent development of a satisfactory process for high temperature coking of heavy residual oils involves the utilization of preheated finely divided solid particles to supply heat requirements. These particles are preferably substantially inert catalytically. Generally speaking, the coke particles formed in the coking process itself are preferred as heat carrying solids to supply requirements for the endothermic coking conversion reaction.

Due to the nature of the product produced in coking, considerable difficulty has been encountered in the building up of deposits in the apparatus as the coker products are cooled and fractionated. Whenever heavy oil fractions are passed through a temperature transition from vapor to liquid, or vice versa, it is difficult to prevent carbonaceous deposits on the apparatus. An important aspect of the successful commercial development of fluid solids coking has been the provision of means for including finely divided solids in a scrubbing system to keep the apparatus clean. This slurry has been recycled directly to the coker. In such recycling, a substantial portion of the gas oil produced is lost.

An object of the present invention is to recover a substantial part of the gas oil which previously has been lost due to the recycle of coker slurry to the coking system. According to the present invention, this slurry is passed to an intermediate zone of a combination fractionator. The vapor overhead from a catalytic cracking operation is fed to the lower part of the fractionator to supply heat requirements. By this means, the heavy gas oil which is a good catalytic cracking feed stock is stripped from the slurry and it can be and preferably is recycled to the catalytic cracker as a clean feed stock.

Another difficulty frequently encountered with commercial fluidized solids coking is the inclusion in the gas oil products of substantial amounts of ash forming materials. Metal constituents, such as nickel, vanadium, etc. are highly injurious to cracking catalysts. Coker gas oil frequently includes substantial proportions of these injurious substances. Attempts have been made to remove these objectionable materials from coker gas oil by severe fractionation and the like. Such fractionation is usually objectionable in that it removes a considerable proportion of valuable feed stock from the net coker product.

According to the present invention, a clean gas oil which is quite suitable for catalytic cracking is obtained without substantial loss in yield.

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The invention has several aspects. For example, the gas oil fraction from the combination fractionator may be combined with gas oil feed from other sources such as a virgin distillation or topping operation. The heavy bottoms from the combination fractionator may be taken either directly to the coker as the sole feed stock or they may be combined with other feeds. Moreover, these heavy bottoms which include the entrained fines used for scouring as described above may be subjected to other operations in addition to and/or prior to the coking operation to recover additional yields of certain constituents such as light and heavy gas oil.

A further advantage of the process is that the solids entrained from catalytic cracking operations may be combined in the heavy bottoms from the combination fractionator and may ultimately be disposed of in the coke product from the coking operation. Other objects and advantages of the invention will become more fully apparent as this description proceeds.

It has been suggested previously in the art that the heat of the vapors from a catalytic cracking operation may be used to assist in fractionation of the total products. For example, the patent to Harding et al. 2,644,785 discloses this concept. It has also been proposed for example, in Keith Patent 2,174,858 to combine a thermal cracking operation and a normal cracking operation so that the products from the latter are used to assist in fractionating the thermal products. The present invention involves a substantial improvement over both of these references and over the prior art in general. Reference will next be made to the accompanying drawings which form a part of this specification.

Figure 1 is a diagrammatic view in elevation of a system involving a fluidized solids coker, a fluidized solids catalytic cracker and a combination fractionator.

Figure 2 is a system like Figure 1, to which has been added a special visbreaker or thermal cracking coil with its own independent fractionator.

Figure 3 shows a further feature in which an initial fractionation still, for example an atmospheric fractionator for crude oil feed is combined in such a way that the coker vapors of lowest boiling range are used to help supply the heat required for initial fractionation. In other respects, this system is substantially the same in principle as those shown in Figs. 1 and 2.

Referring now in detail to the drawings in Fig. 1, reduced crude is fed through line 11 to a conventional fluidized solids coker 13. The details of the coker form no part of the present invention but it may be and preferably is of the general type disclosed in the application of Pfeiffer et al., Ser. No. 375,088, filed August 19, 1953. In this system, hot fluidizable solids such as finely divided coke are fed through a line 15 to a fluidized bed 17. The feed is injected into this bed through one or more spray nozzles and the product vapors pass upwardly through suitable solids separating equipment such as cyclones, not shown. Additional coke is formed and deposited upon the solids and this may be circulated through a return line 19 to a burner or regenerator, not shown. Part of the product coke may, of course, be withdrawn and used for fuel or sold for other purposes.

The effluent vapors from the coking operation contain heavier oils which tend to cause considerable difficulty because they form deposits in the overhead apparatus. To prevent the formation of such deposits, the coker is so operated that appreciable quantities of the finely divided solids such as coke particles which are preferably substantially inert catalytically are passed overhead with the vapor products. These particles serve to keep the apparatus clean by reason of mechanical abrasion and scrubbing. In the overhead portion of the apparatus indicated at 21, there are provided fractionating plates

or trays 23 of suitable type. These separate the overhead into two or more fractions, preferably at least 3. As seen in Fig. 1, the light vapors and gases pass overhead to outlet line 25. A light or medium gas oil is taken off at an intermediate section through line 27 and heavy gas oil with the solid matter included to form a slurry may be taken off near the bottom through a line 29. The latter fraction is conducted to an intermediate or lower intermediate zone of a combination fractionator 31. The lighter and cleaner gas oil taken off through line 27 may be conducted into a catalytic cracking unit of conventional type indicated at 35. The overhead light product gases and vapors from line 25 may be taken to suitable separating and recovery equipment or they may be conducted into the bottom part of fractionator 31 as indicated by the dotted line 37.

Gas oil fed from line 27 together with other gas oil which may be fed through a line 39, or recycled feed through line 41, is introduced through line 43 into the catalytic cracker 35. This unit, as shown, is of conventional type and preferably utilizes a fluidized bed of cracking catalyst. The operation of this unit per se is well known and needs no description. Catalyst regeneration facilities are provided but are not shown in the drawing.

The catalytic cracker vapors are passed overhead through suitable conventional separating equipment into line 45. This line conducts the vapors to the bottom or near the bottom of fractionator 31 so that their heat is utilized in fractionating the slurry supplied from line 29. The overhead vapors and gases from the coker supplied through line 25 may be introduced through branch line 47 and under control of valve 49.

From the combination fractionator, overhead gases and/or like products may be taken off through lines 51 and 53. A cut of intermediate boiling point such as a heating oil, kerosene, diesel fuel or the like may be taken off through line 55. Gas oil suitable for catalytic cracking feed stock is taken off at line 57 which connects to line 41 and is fed into the catalytic cracker.

Bottoms may be removed from the fractionator through bottom outlet line 59 through which they are recycled to the coker. A branch feed line 61 may be provided to feed part of the coker feed into a lower portion of the coker bed. The products returned through line 59 include entrained solids carried to the fractionator through line 29. They may also include small amounts of finely divided catalyst particles entrained in the catalytic cracker overhead line 45.

Part of the recycled heavy bottoms with entrained solids may be withdrawn from the system through outlet line 63 under control of valve 65. These products may be burned as fuel or otherwise disposed or when it is not desired to recycle them to the coker.

Referring to Fig. 2, the separation is substantially the same as in Fig. 1 and similar reference characters have been applied to identical parts. The only substantial differences are that instead of taking the fractionator bottoms back directly to the coker, there are first passed through thermal visbreaking or thermal cracking operations. As indicated in Fig. 2, line 59A which corresponds to line 59 of Fig. 1 leads to a visbreaker coil 71 in a furnace 73. Here the oil is visbroken or cracked at high temperature and at suitable pressure before being passed on for further operations. The products thus thermally cracked or visbroken may be recycled in part to the fractionator through line 75 under control of valve 77. In this event, the combination fractionator unit 31 serves to fractionate the thermally cracked products. Alternatively, a small fractionator 79 may be provided to which the thermally cracked products are fed through line 81 under control of valve 83. Various products may be taken off through lines 85, 87, 89 and the bottoms returned through line 91 which connects with line 59-B. Outlet line 63, with control valve 65, makes it possible to withdraw heavy products from recycle if desired. A line

95 under control of valve 97 makes it possible to bypass the fractionator with all or part of the thermally cracked or visbroken material if desired. In other respects, the operation is the same as in the case of Fig. 1.

Referring now to Fig. 3, the same general type of operation is contemplated except that the original crude fractionation is included in the combination and the vapor products from the coker are used to assist in this fractionation.

Crude oil, or a reduced crude which has been topped, if desired, for making virgin gasoline, etc., is fed through line 111 into an atmospheric fractionator 112. A heating oil fraction may be removed through line 113 and the overhead products including gas and light naphtha are taken off through line 114. A valve 115 makes it possible to take these products directly to suitable separating or fractionating equipment through line 116. Alternatively and preferably, the fraction is passed through line 117 under control of valve 118 into a conventional hydroformer 120.

The hydroformer 120 may be of any suitable or conventional type. As shown here, it involves a two-stage fixed bed arrangement with means not shown for suitably heating the feed between stages and furnishing hydrogen gas thereto. These features are well known in the art. The eventual hydroformate product is taken off through line 121, along with gas. It usually is not desirable to recycle this material to a fractionator although it has suitable heat content. Hydrogen content of the gas is usually quite high, and it is preferable to clean up the hydrogen and recycle it to assist in the reforming operation.

The bottoms from the atmospheric fractionator are taken from line 125 to a point in the lower intermediate section of combination fractionator 131. This fractionator corresponds to the units 31 in Figs. 1 and 2. If desired, the bottoms fraction from the atmospheric still or fractionator 112 may be taken through a preheater or furnace 127 to supply additional heat to the fractionator.

The products from the combination fractionator 131 may consist of a naphtha and gas fraction taken overhead through line 151, a heating oil fraction from line 153 and a gas oil fraction from line 157. The latter is a good catalytic cracking feed stock and is taken directly to a catalytic cracking unit 135 which corresponds in all respects to the units 35 of Figs. 1 and 2. Here the gas oil is converted to an overhead vapor and gas fraction plus a carbonaceous residue which is deposited on the catalyst. The overhead products are taken through line 145 and returned to the bottom of the combination fractionator as in the other modifications previously described.

The bottoms from the fractionator 131 are taken through line 159 to a coker 160. Here they are converted, as in the previously described modifications. Overhead vapors and light hydrocarbons are taken from the coker through line 162 into the bottom of the atmospheric fractionator 112. There the coker vapors facilitate distillation of the crude by providing heat and diluent gas to lower the hydrocarbon partial pressure. A further advantage is that a separate fractionation system is avoided on the coker products from line 162. These are handled in mixture with virgin products through hydroforming, etc. The heavy gas oil containing entrained heavy ends and solid particles is in the form of a slurry. This slurry is passed through line 129 into an intermediate or lower intermediate zone of the combination fractionator. Here, the valuable gas oil components are stripped by the vapors from the catalytic cracking unit supplied through line 145, as previously described.

The bottoms with entrained coke particles and catalyst particles which may be carried over from the catalytic cracker are recycled through line 159 to the coker. In

this modification the line 159 is shown as dividing into a plurality of branches 171, 172 under control of valves 173 and 174 for injection at spaced points into the fluid solids bed of the coker. Hot solids are supplied through line 175 and the spent coke is returned to a heater or regenerator not shown through line 177. Product coke may be withdrawn through line 179, as is well known in the art.

It will be appreciated that the process of the invention provides for upgrading heavy oil by feeding that heavy oil to a coker to produce a light low boiling fraction and a heavy gas oil fraction in which heavy ends and ash forming components are included. Other fractions, such as light gas oil, may be produced if desired. The heavy gas oil fraction, with the components which make it unsuitable for direct catalytic cracking, and with entrained carbonaceous residues, is passed in the form of a slurry to an intermediate part of the combination fractionating zone.

Poor fractionation of coker gas oil results in severe degradation of its cracking quality. This is illustrated by the following laboratory cracking data on experimental coker gas oils.

Feed.....	Recycle, Elk Basin	Once- through, Hawkins
Cat. cracking yields:		
Dry gas, weight percent.....	8.8	8.8
C ₄ -430° F., vol. percent.....	33.5	42.0
Gas oil, vol. percent.....	50.0	50.0
Coke.....	13.1	6.0

Carbon make is doubled for the same conversion with the feed from recycle coking. This is due largely to degradation of the gas oil left in the slurry, which is recycled through the coker. By returning the slurry from the coker scrubber to the bottom of the catalytic fractionator, gas oil is recovered from the slurry before it is recycled to the coker. It is possible to do a better fractionation job in the catalytic fractionator, because this equipment is far less subject to coke deposition.

In many cases, it may be desirable to add the total coke overhead vapors to a combination unit fractionator. This will allow increasing the cut point on the bottoms, since additional heat and vaporizing gases are being added.

In many cases, the heavy coker naphtha will be hydroformed. This would normally require a separate splitter tower to segregate the heavy coker naphtha. This expensive tower can be eliminated by introducing the coker vapors into the catalytic cracker fractionator or the crude distillation tower, as shown in one of the alternates described above.

A gas oil which is of suitable quality, is catalytically cracked to produce hydrocarbon vapors. This gas oil may be of extraneous origin, or it may be that produced in coking operation. It may also be produced simultaneously in an atmospheric still or in a separate vacuum still. Often the coker gas oil per se is insufficient in quantity to operate the cracking unit and to maintain a good balance. Hence, extraneous gas oil, e.g. virgin gas oil, ordinarily will be added so as to produce substantial quantities of cracked hydrocarbon vapors. The heat content of these vapors is used for fractionation by passing them to a lower part of the fractionation zone to strip the valuable gas oil from the slurry which comes from the coker. Thereby a gas oil of suitable quality for catalytic cracking is recovered from the heavy coker product.

In its apparatus aspects, the invention comprises a combination of a coker means for separating an overhead fraction and a heavy gas oil fraction which contains the impurities described above. Usually an intermediate fraction suitable as a direct catalytic cracking feed stock is produced at the same time. Means are provided for

carrying finely divided solid particles into the overhead system to keep it clean by scrubbing and abrading incipient carbonaceous deposits from the apparatus surfaces. These particles, which eventually wind up in a slurry of heavy gas oil and heavy end components, are then passed by suitable means into the intermediate zone of the combination fractionator.

Means are provided for returning from the fractionator a bottoms fraction which includes the objectionable heavy tar components and the solids which were carried into the fractionator by the slurry. These materials also include the bulk of the ash-forming or metallic contaminants which cause difficulty in catalytic cracking. All of these materials plus entrained catalyst fines from the catalytic cracking operation are returned to the coker. Means are provided, however, for withdrawing some of these materials from recycle, if desired. Catalytic cracking means are, of course, included to produce vapors of the naphtha boiling range and means are provided for returning these vapors with their high heat content to the lower part of the combination fractionator to supply heat thereto.

It will be appreciated that numerous variations may be made within the spirit of the invention and it is intended to cover such so far as the prior art permits.

The usual operating conditions of pressure, temperature, feed rate, solids recycle rate, etc., as well known in the prior art, will normally be maintained. Coking temperatures are usually between 800 and 1000° F. Operating pressures are preferably 0 to 50 p.s.i.g. for both cracking and coking. These and other variables can be adjusted within limits well known to those skilled in the art without departing from the spirit or purpose of the invention.

What is claimed is:

A process for converting heavy residual hydrocarbon oil to more valuable products including naphtha, which comprises feeding the oil to a fluid coking zone, contacting the oil in said coking zone with finely divided preheated coke particles, which are substantially inert catalytically, for a sufficient period of time and at a cracking temperature sufficiently high to convert the oil to vapor products containing naphtha and carbonaceous residue, passing said vapor products including high boiling heavy ends and finely divided solid particles to a scrubbing zone, forming in said scrubbing zone a slurry of said solid particles and said high boiling heavy ends which also includes a heavy gas oil fraction containing ash-forming constituents unsuitable for direct passage to a catalytic cracking step hereinafter referred to, recovering vaporous products including naphtha overhead from said scrubbing zone, passing said slurry to an intermediate section of a fractionating zone, recovering a clean gas oil fraction from said vapors in said scrubbing zone which is suitable for catalytic cracking, passing said last-mentioned clean gas oil fraction to a catalytic cracking step to form cracked vapors containing naphtha, introducing said last-mentioned cracked vapors without substantial cooling into said fractionating zone below the region of introduction of the slurry to strip gas oil from said slurry and which gas oil is of suitable quality for said catalytic cracking step, recovering said last-mentioned gas oil and passing it to said catalytic cracking step, recovering naphtha from the upper portion of said fractionating zone, returning the bottoms from said fractionating zone, including residual portions of said slurry to said fluid coking zone, reheating coke particles by partial combustion and returning them to said fluid coking zone to supply heat thereto.

References Cited in the file of this patent

UNITED STATES PATENTS

2,644,785	Harding et al.	July 7, 1953
2,717,862	Murphree	Sept. 13, 1955