Dec. 2, 1958 A. VOORHIES, JR 2,862,870

PROCESS FOR UPGRADING RESIDUA

Filed Nov. 23, 1953 2 Sheets-Sheet 1

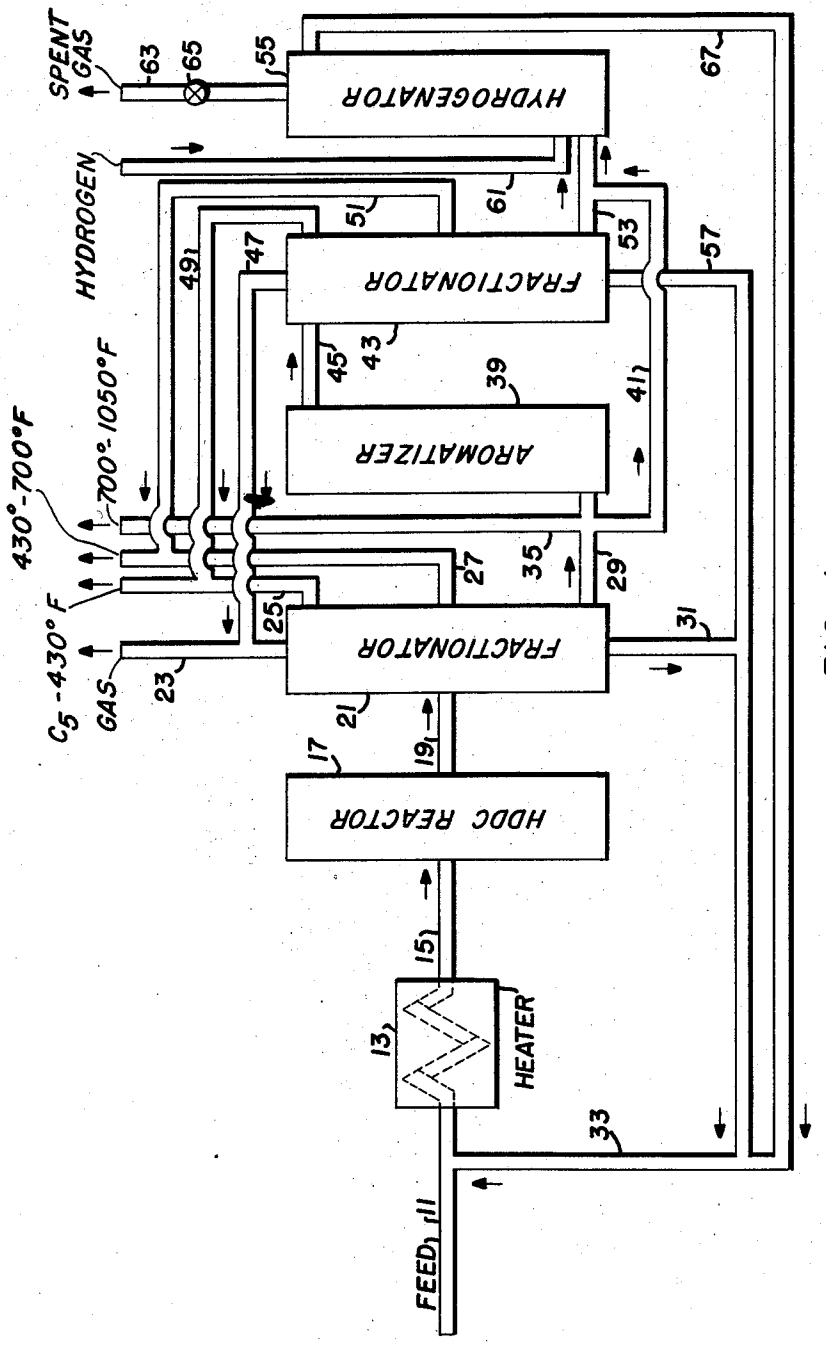


FIG. - 1

Alexis Voorhies Jr. Inventor

By Edwin M. Thomas Attorney

Dec. 2, 1958 A. VOORHIES, JR 2,862,870

PROCESS FOR UPGRADING RESIDUA

Filed Nov. 23, 1953 2 Sheets-Sheet 2

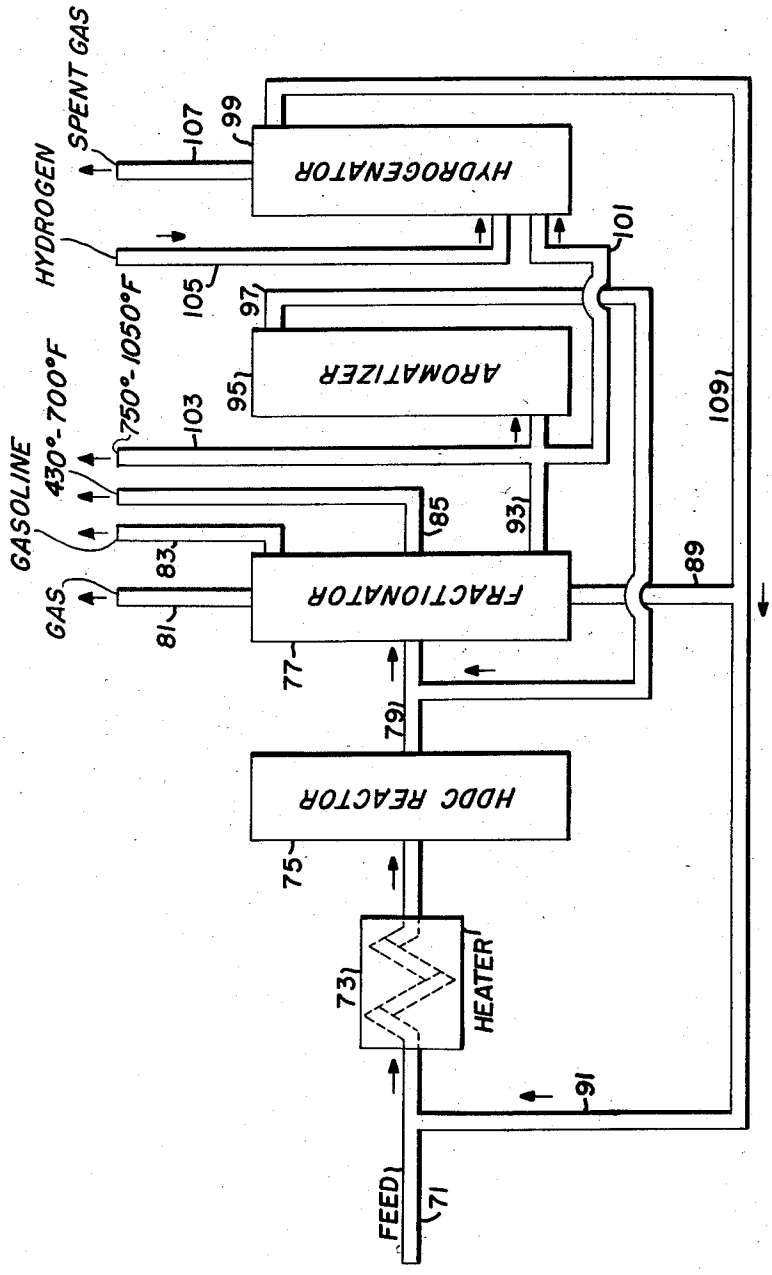


FIG-2

Alexis Voorhies Jr. Inventor

By Edwin M. Thomas Attorney

United States Patent Office

2,862,870

Patented Dec. 2, 1958

2,862,870

PROCESS FOR UPGRADING RESIDUA

Alexis Voorhies, Jr., Baton Rouge, La., assignor to Esso Research and Engineering Company, a corporation of Delaware

Application November 23, 1953, Serial No. 393,617

3 Claims. (Cl. 208—56)

The present invention relates to an improved process for converting residua such as the heavy residuum resulting from refining of petroleum and analogous material. The feed stock may be a petroleum residuum of high boiling range or it may be a total crude of the same general characteristics. Coal tar, shale oil and the like or the heavy ends thereof may be used as the feed.

In the prior art numerous proposals have been made for converting heavy residual oils to more volatile and more valuable products. As a rule, these heavy feed stocks have been converted by coking, that is, by subjecting them to high temperature treatment for a sufficient period of time to crack part of the feed to lighter products and to degrade a portion to coke with the accompanying production of gas. The gas and coke so produced are normally of less value than the motor fuel and gas oil products. It is therefore preferred to produce as much motor fuel and gas oil as possible with a minimum conversion to gas and coke. An object of the present invention is to accomplish such conversion.

It has also been proposed recently to convert heavy residual oils of the type mentioned above by the use of a hydrogen donor diluent. The feed and the diluent are subjected to mild thermal treatment which results in cracking the feed to obtain a good distribution of products. This process has been called for brevity the hydrogen donor diluent cracking process or more briefly the HDDC process. The present invention involves a specific improvement in the HDDC process.

According to the present invention a suitable feed stock such as heavy petroleum residuum is combined with a hydrogen donor diluent, to be described, and the mixture is preheated to a suitable temperature, usually between about 750° and 1000° F. A preferred temperature is between about 800° and 900° F. The mixture is passed into a reactor where the ingredients remain for a time and at a temperature suitable for accomplishing the hydrogen donor diluent cracking. This cracking results in the production of substantial proportions of gasoline, of light gas oil boiling between about 430° and 700° F., of heavy gas oil boiling between about 700° and 1050° F., and a bottoms fraction boiling above about 1050° F. The motor fuel and light gas oil products are taken to storage or to further processing such as hydroforming or catalytic cracking. A portion of the 700 to 1050° F. heavy gas oil fraction also may be taken to a catalytic cracking operation. Part of the same fraction is treated according to the present invention, to convert it substantially to armatic products for a purpose to be described. The remainder of the 700 to 1050° F. fraction is passed through a hydrogenator.

The portion of the heavy gas oil which is treated to convert it to a substantial degree to aromatics is contacted with a suitable catalyst for this purpose. A highly satisfactory process for aromatizing involves an operation in the nature of hydrocracking wherein a suitable catalyst is used and hydrogen gas is evolved. Such hydrocracking processes preferably use a chromia alumina catalyst and are operated at a pressure of 50 to 500 p. s. i. g. and at a temperature between about 900 to 1050° F. with a feed rate of 0.6 to 0.9 w./hr./w. for a fixed or fluid bed process. A suitable catalyst consists of 95% of alumina and 5% of chromia.

Typical data from an aromatizing process are listed below in Table I.

Table I

Operating Conditions	East Texas Light Gas Oil	Wide Cut Paraffinic Gas Oil	West Texas Wide Cut Gas Oil
Reactor Temperature, °F	975	975	975
Reactor Pressure, p. s. i. g.	100	100	100
Feed Rate, W./Hr./W	0.72	0.72	0.72
Hydrogen Rate, C. F./B.	3,000–5,000	3,000–5,000	3,000–5,000
400° F.+Gas Oil, Vol. Percent on feed	31	30	34
Gravity, °API	14.4	15.4	15.3
Aniline Point, °F	34	52	54
Feed Stock Inspections:			
Gravity, °API	33.7	30.3	29.2
Aniline Point, °F	172	192	165

The products from the aromatizing, or more specifically hydrocracking, process described contain considerable proportions of condensed ring aromatics which are excellent hydrogen donor materials when partially hydrogenated. The decrease in the aniline point indicates the increase in aromatics. The aromatization product contains 65 to 80 percent of aromatic hydrocarbons of which about one-half are of the desired bicyclic or higher condensed ring type. The products from the aromatizer are fractionated into the same cuts, temperature-wise, as the products mentioned above. Thus products boiling in the gasoline range may be added to the gasoline product from the first reactor and the light gas oil may be added to the primary light gas oil.

The 700° to 1050° F. aromatized product is passed to a hydrogenator along with a portion of the original heavy gas oil (700° to 1050° F. cut) mentioned above. These combined materials are hydrogenated partially but not completely by treatment with 200 to 2000 s. c. f. of hydrogen per barrel of feed to the hydrogenator. The precise method of hydrogenating forms no part of the present invention but a suitable process involves the use of a standard hydrogenating catalyst, preferably of the sulfur insensitive type, e. g. molybdenum sulfide, or nickel-tungsten sulfide. Hydrogenation is carried out at moderate temperatures (600–800° F.) and at suitable pressure such as 200 to 1000 pounds per square inch.

It will be understood that the purpose of the aromatizing step is to provide continuously a make-up stream of the most desirable type of aromatics. Such a make-up stream is necessary because the hydrogen donor reaction is not completely selective and the distillation of products in the primary fractionator is not completely selective. Otherwise the desired condensed ring products would circulate indefinitely within the system, picking up hydrogen in the hydrogenator and releasing it in the HDDC reactor. However, a small proportion of the total recycle through the hydrogenator is sufficient to keep the system in balance. Thus 5 to 10% of the heavy gas oil fraction, 700° to 1050° F., may be passed through the aromatizer and the 700° to 1050° F. fraction of the aromatized product, which may amount to only about half the feed to the aromatizer, is combined with the bulk of the heavy gas oil for hydrogenating and recycling to the HDDC reactor.

In a typical example, 10,000 B./D. of residuum feed are mixed with 20,000 B./D. of a recycle stream, and after suitable preheating the mixture is contacted in the reactor at 800–900° F. and at a pressure that may be varied from substantially atmospheric to 500 p. s. i. g., and

higher. The recycle stream contains the hydrogen donor as will be described subsequently. The converted products pass from the reactor to a still where conventional separation is made to give gas, gasoline, a 430–700° F. cut, a 700–1050° F. cut, and a 1050° F.+ bottoms. The 700–1050° F. cut is split into two streams. The larger stream consisting of 14,500 B./D. is sent to a low pressure hydrogenation step before recycling to the reactor. The smaller stream of 700–1050° F. material comprising 1000 B./D. is sent to the "aromatizer" for the purpose of producing a 700°–1050° F. cut consisting to a large extent of polycyclic, condensed ring aromatics. The product from the aromatizer goes to a small still where the products are separated into gas, gasoline, a 430–700° F. cut, a 700–1050° F. material, and 1050° F.+ bottoms. The small amount of 1050° F.+ bottoms is mixed with the 500 B./D. of 1050° F.+ material from the primary still and is included in the 20,000 B./D. of recycle material which enters the process. The highly aromatic 700–1050° F. cut consisting of 500 B./D. is blended with the 14,500 B./D. of primary 750–1050° F. cut previously mentioned, and this combined feed of 15,000 B./D. goes to the hydrogenation step.

The invention will be more clearly understood by reference to the attached drawings which illustrate diagrammatically two preferred embodiments thereof. Figure 1 shows schematically a system incorporating the features mentioned above and Figure 2 shows an alternative and somewhat simplified system.

Referring first to Figure 1 the feed, a suitable petroleum residuum for example, enters through line **11** and passes through a suitable heater, for example, a coil **13** where its temperature is raised to between 750 and 1000° F. A preferred temperature is between 800° and 900° F. A recycle stock described below is preheated simultaneously and the combined products are passed through line **15** into the HDDC reactor vessel **17**. In this vessel the reaction is allowed to continue for a suitable period of time which may range from ¼ to 4 hours or more. The products from reactor **17** pass through line **19** to a fractionator or a distillation unit **21**. Here the C_4 and lighter gases are taken overhead through line **23**. A motor fuel fraction from C_5 to about 430° F. passes out through line **25**. The 430° to 700° F. light gas oil passes off through line **27** and the 700° to 1050° F. heavy gas oil through line **29**. A bottoms fraction passes through line **31** to return lines **57** and **33** which recycle it to the heater **13**.

The heavy gas oil fraction is divided approximately into two or more parts depending upon the product distribution desired. Thus a portion may be taken through line **35** as a product for direct use or for feed stock to a catalytic cracker. A minor portion, for example 5 to 10%, is led through line **29** to an aromatizing zone **39**. A major fraction is carried through line **41** to pass through the hydrogenator and recycle with the feed as will be described.

The fraction passed to the aromatizer is treated with a suitable aromatizing catalyst at a temperature between 900 and 1050° F. under pressure which may be between 50 and 500 p. s. i. g. The products from the aromatizer are taken to a fractionator **43** through line **45**. Here a gas fraction which may include hydrogen is carried overhead through line **47** to combine with the gas in line **23**. When this gas is rich in hydrogen, as it is in some cases, the hydrogen may be returned to the hydrogenator described below. The products from fractionator **43** which boil in the motor fuel range are taken off through line **49** and the light gas oil through line **51** to combine respectively with the products in lines **25** and **27**.

The 700° to 1050° F. fraction from the fractionator **43** is passed through a line **53** to the hydrogenator **55**. A bottoms fraction from fractionator **43** is taken through line **57** to recycle with the bottoms from fractionator **21** to line **33**.

The aromatized heavy gas oil fraction is combined with the heavy gas oil from line **41** and by line **53** is transferred to the hydrogenating unit **55**. This contains a suitable hydrogenating catalyst such as molybdenum sulfide or other suitable catalyst of known type. Hydrogen gas, or a mixture rich in hydrogen, is supplied through line **61** to the hydrogenator, spent gas being taken off overhead in line **63** through a suitable valve **65**. It may be and frequently is desirable to recycle the spent gas from line **63** to the hydrogen feed line **61** to conserve hydrogen.

The hydrogenator **55** is operated under such conditions as to partially but not fully hydrogenate the condensed ring aromatic constituents entering through line **53**. As noted above these constituents are considerably enriched by passing part of the hydrogenator feed through the aromatizing operation at **39**.

The hydrogenated material is taken from hydrogenator **55** through line **67** to combine with the refluxing bottoms from the fractionators. These combined materials are added to the feed and passed through the heater **13** to the HDDC reactor where the cycle is repeated. With an average petroleum residuum feed stock and with the various streams divided in the proportions suggested above, the process of this invention may yield about 5% by volume of gasoline, 20% of 400° to 700° F. light gas oil and 70% of 700° to 1050° F. heavy gas oil per pass. The overall efficiency will vary with the division of the 700° to 1050° F. stream from line **29**. These yields are merely illustrative and will vary to some extent with the quality of the original feed stock. In general conversion of approximately 95% may be expected. By recycling, the bottoms may be treated to extinction. Gas yields are relatively low.

Referring now to Figure 2 the same general process is shown except that the effluent from the aromatizer is recycled to the primary fractionator. This eliminates the need for a secondary fractionator **43** as shown in Figure 1.

Briefly, feed enters through line **71** to heater **73** and HHDC reactor **75**. The reaction products are taken to fractionator **77** through line **79**. The gas, gasoline, light gas oil, and heavy gas oil are taken off respectively through lines **81**, **83**, **85**, and **93**. Bottoms from fractionator **77** are recycled through line **89** to return line **91**.

A portion of the 700° to 1050° F. heavy gas oil passes directly through line **93** to the aromatizer **95** from which the total products are recycled through line **97** to the fractionator **77**. The remainder of the 700° to 1050° F. gas oil is taken to the hydrogenator **99** through line **101** except that a portion may be withdrawn as product through line **103** if desired. If will be understood that in all these lines, and in the lines of Figure 1 suitable valves will be provided as needed.

The heavy gas oil taken to the hydrogenator **99** through line **101** includes an aromatized portion recycled through the fractionator. This material, together with gas oil which has not been aromatized, is partially hydrogenated, hydrogen being supplied through a line **105** and spent gas removed through a line **107** as in Figure 1.

The partially hydrogenated feed is recycled through line **109** to combine with the fractionator bottoms in line **91** and both are taken through the heater with the fresh feed to the HDDC reactor.

It will be understood that various modifications may be made in the arrangement and use of the systems described in detail above without departing from the spirit of the invention.

What is claimed is:

1. The process of upgrading heavy oil to produce lower boiling products which comprises combining with one volume of feed one to four volumes of a partially hydrogenated recycle stock obtained as described hereinafter, heating the combined feed and recycle stock to a temperature within the range of 750° to 1000° F., passthe heated mixture into a reaction zone and reacting for

a sufficient time to transfer hydrogen from the recycle stock to the feed and to crack the mixture, fractionating the products of the reactor to obtain a motor fuel fraction, a light gas oil fraction and a heavy gas oil fraction, aromatizing part of said last mentioned fraction, partially hydrogenating the aromatized and unaromatized portions of said heavy gas oil fraction and recycling the partially hydrogenated fraction to the feed.

2. Process according to claim 1 wherein the feed and recycle stock are preheated to a temperature between 800° and 900° F.

3. The process of converting heavy residual oil to products of motor fuel and gas oil boiling range which comprises: combining with one volume of feed one to four volumes of a partially hydrogenated recycle stock obtained as described hereinafter, heating the combined feed and recycle stock to a temperature between about 750° to 1000° F., and reacting this mixture for a period of about ¼ to 4 hours to transfer hydrogen and cause hydrogen donor diluent cracking of the feed, fractionating the cracked products to separate therefrom a heavy gas oil fraction boiling within the range of about 700°

to 1050° F., aromatizing about 5 to 10% of said heavy gas oil and fractionating the aromatized product, segregating a first fraction of the aromatized product boiling above about 1050° F. and recycling it to the said reaction zone, segregating a second fraction of the aromatized product boiling in the range of about 750° to 1050° F. and combining said second fraction with at least a part of the non-aromatized heavy gas oil, partially hydrogenating said combined heavy gas oils, and recycling them to the reaction zone.

References Cited in the file of this patent

UNITED STATES PATENTS

2,249,337	Visser	July 15, 1941
2,290,033	Burk et al.	July 14, 1942
2,426,929	Greensfelder	Sept. 2, 1947

OTHER REFERENCES

Sachanen: Chemical Constituents of Petroleum (1945), page 223, Reinhold Publishing Corp.