

Aug. 25, 1959

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CATALYTIC CRACKING PROCESS

2,901,413

Filed April 26, 1955

2 Sheets-Sheet 1

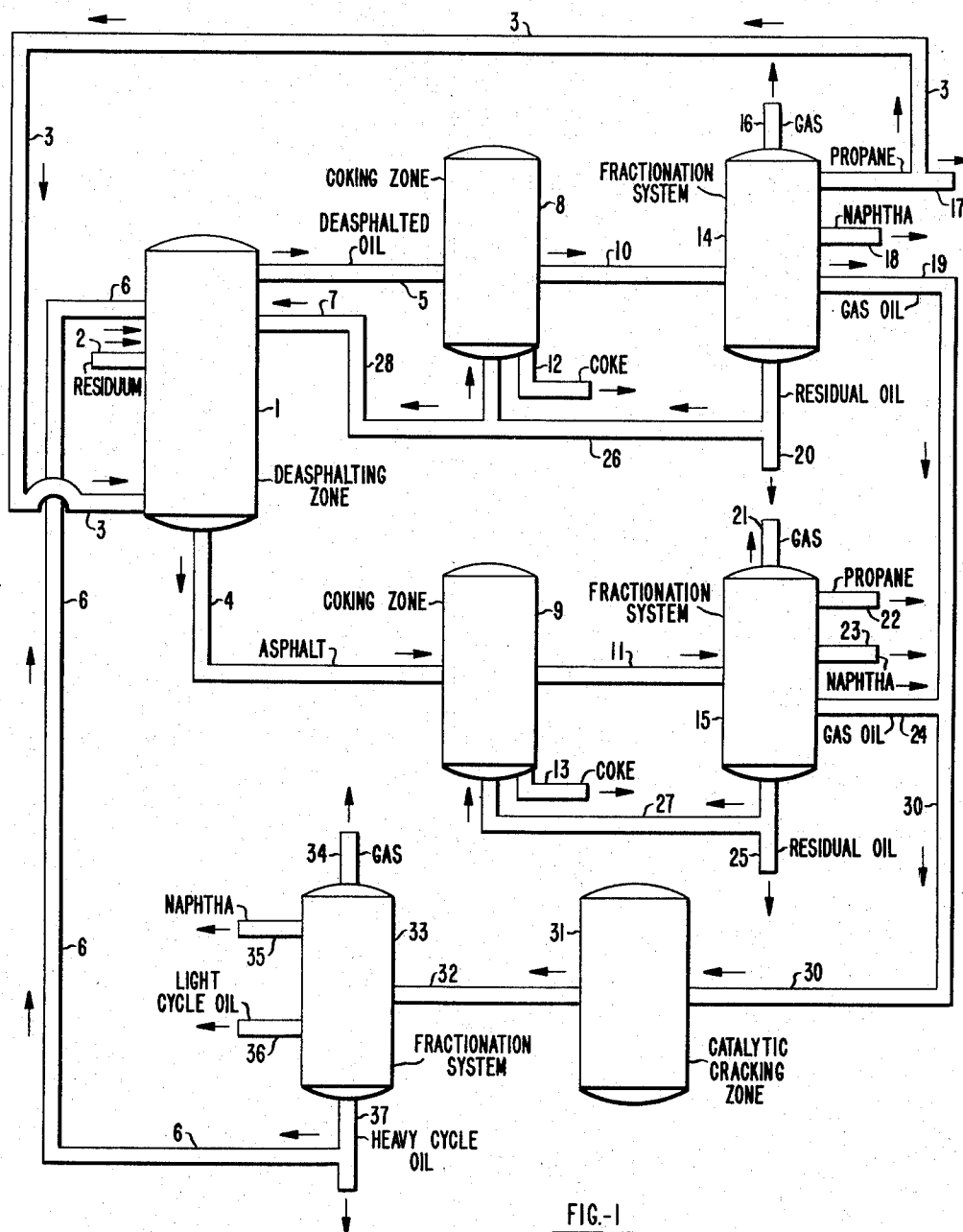


FIG. 1

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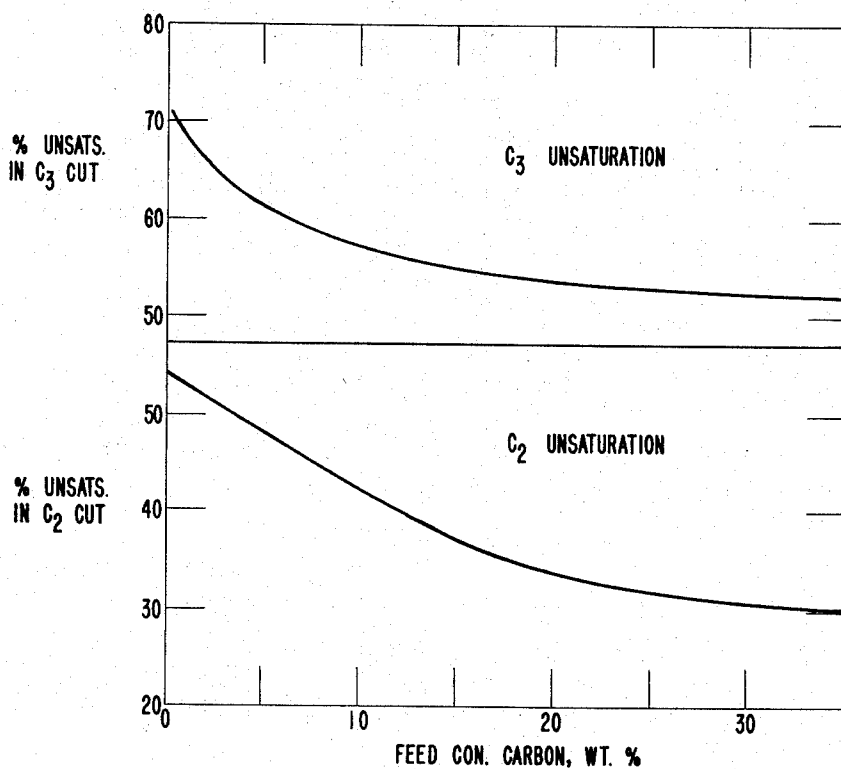


FIG.-2

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COMBINATION DEASPHALTING, COKING, AND CATALYTIC CRACKING PROCESS

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Application April 26, 1955, Serial No. 503,988

4 Claims. (Cl. 208—55)

This invention relates to conversion of heavy petroleum residual oils to distillate products by processing steps including deasphalting and coking. The invention provides a processing technique combining these basic refining operations so as to particularly maximize the yield of unsaturated hydrocarbons useful for chemical applications and so as to maximize the yield of high quality catalytic cracking feed stocks.

The development of markets for petroleum oil products has heretofore been characterized by ever growing demands for high quality motor fuel and other distillate products without a proportional increase in uses for residual petroleum oil products. This circumstance has dictated the need, from an economic and conservation viewpoint, to provide refining operations capable of increasing distillate products, and particularly gasoline production, from crude oil while minimizing the quantities of residual oil produced. A number of attractive and alternative refining processes are being developed adapted to permit upgrading of heavy petroleum residues into distillate stocks.

One process which has shown particular promise involves the deasphalting of a petroleum residue providing a deasphalted oil of good cracking characteristics. U.S. Patent 2,700,637 issued January 25, 1955, to W. T. Knox, Jr., particularly discloses and claims an attractive deasphalting process for residual oils adapted to provide high quality cracking feed stock so as to permit ultimate production of valuable distillate products from an initial residual oil feed.

Another desirable process for upgrading residual fractions is the coking process and particularly a fluidized coking operation. In this process a heavy petroleum residue is contacted with hot solids so as to convert the residue into coke, gas oil suitable for catalytic cracking, motor fuel, and gas products.

Each of the deasphalting and coking processes referred to are in their own right valuable refining operations for upgrading residual oils. These processes have heretofore been considered to be alternates, permitting a refiner to choose or select the particular process to be employed. The present invention is based on the discovery that these processes of deasphalting and coking can be attractively employed in combination so as to provide substantial and unexpected advantages as regards the amount and quality of distillate products obtainable, as well as the amount of light olefins produced. The present invention is particularly characterized by an integration of deasphalting and coking steps applied to a residual oil so as to substantially increase the proportion and amount of ethylene and propylene obtained. Maximizing production of these unsaturated hydrocarbons is particularly desirable and economically valuable due to the utility of these compounds in chemical processes. A second objective of this invention is to employ a combination of deasphalting and coking so as to substantially improve the quantity and quality of catalytic cracking feed stock derived from the residual oil feed. In this connection, the invention

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entails a combination of deasphalting, coking, and catalytic cracking, which permits obtaining greater yields of motor fuel products from a residual oil than heretofore obtainable.

The present invention is based on appreciation of certain basic characteristics of the processes involved which have not heretofore been recognized. In connection with the coking operation, it has now been found that the total dry gas produced in coking a residual oil is substantially independent of the feed stock employed with particular reference to the Conradson carbon content of the feed stock. In general, somewhat more dry gas is produced from residual oils having high Conradson carbon contents, but the difference is not great. Furthermore, and as a critical feature, the proportion of dry gas produced in coking varies substantially linearly with the Conradson carbon content of the residual oil which is subjected to coking. However, it has been found that the proportion of C_2 and C_3 unsaturated hydrocarbons present in coked product streams varies appreciably with the Conradson carbon content of the coking feed stock. Furthermore, and as a critical feature, which is the basis of this invention, the variation in the proportion of these constituents with the Conradson carbon content of the feed stock is a non-linear relation. As will be developed, it follows from these basic principles that unique advantages are obtained by splitting a coking feed stock into low and high Conradson carbon fractions and subjecting these fractions to separate coking. By so dividing the feed stock to a coking operation, it is possible to achieve the same total gas production while maximizing the production of unsaturated hydrocarbons in accordance with the principles identified.

Suitable division of a coking feed stock into low and high Conradson carbon fractions is obtained in accordance with this invention by subjecting the coking feed stock to a deasphalting operation. This serves to provide a deasphalted oil having a low Conradson carbon content and an asphalt having a high Conradson carbon content. Consequently, by separately coking the deasphalted oil and the asphalt, the desired production of increased amounts of unsaturated hydrocarbons is obtained.

This combination of deasphalting and coking is also particularly desirable as regards the amount and quality of the gas oil fraction of the coked products. In general, about one-half of the products of coking a residual oil constitute a gas oil adaptable for catalytic cracking to motor fuel products. In considering use of the gas oil coker product for catalytic cracking, it becomes important to obtain a gas oil having desirable catalytic cracking characteristics. In this connection the Conradson carbon content of the gas oil is particularly important since the amount of carbon deposited on the catalyst used in catalytic cracking is a direct function of the Conradson carbon content of the cracking feed. Because of this factor it is necessary to obtain coker gas oil having the lowest possible Conradson carbon value. In addition, it is necessary to obtain a coker gas oil having low concentrations of metal contaminants. It has recently been appreciated that nickel, vanadium, and iron compounds normally occurring in crude petroleum oils are inevitably carried over into heavy gas oil distillates desirable for use in catalytic cracking. Presence of these metal contaminants severely affects the catalysts used in catalytic cracking, so as to adversely change product distribution as a result of cumulative buildup on the catalyst.

The present invention is particularly adapted for producing a coker gas oil of superior cracking characteristics by virtue of low Conradson carbon content and low metal contaminant content. The combination of de-

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asphalting and coking provides these objectives in view of the nature of the coking and deasphalting process. Coking by itself is capable of converting a high Conradson carbon feed stock to a low Conradson carbon gas oil. However, coking by itself is not adapted for complete elimination of metal contaminants, and heavy boiling coker gas oils normally have sufficient concentrations of metal contaminants so as to limit their value as catalytic cracking feed stocks. This problem can be met by adjusting the end point of the coker gas oil product in the range of about 900 to 1000° F., so as to minimize presence of metal contaminants. However, this narrowing of the boiling range of the gas oil results in decreasing the amount of gas oil usable for catalytic cracking. A deasphalting process on the other hand serves to convert a high Conradson carbon feed stock to a low Conradson carbon gas oil having a substantially reduced content of metal contaminants. As a result of these characteristics of coking and deasphalting processes, the combination of these processes in accordance with this invention gives maximum yield of gas oil cracking feed stock of superior value for cracking by virtue of low Conradson carbon content and low concentration of metal contaminants. In this manner the present invention alternatively permits obtaining coker gas oils of markedly superior value for catalytic cracking or substantially greater yields of catalytic cracking feed stock of comparable cracking characteristics.

In order to fully describe the nature of this invention, the essential features of the invention will be described with reference to the accompanying drawings, in which:

Figure 1 diagrammatically presents a specific and preferred embodiment of the invention entailing an integrated deasphalting, coking, and catalytic cracking operation, and

Figure 2 graphically illustrates the relation between production of C₂ and C₃ unsaturated hydrocarbons with respect to the Conradson carbon content of a coking feed stock.

In Figure 1, the basic steps of this invention are illustrated with reference to a particular combination of deasphalting, coking, and catalytic cracking processes. Each of these processes may be conducted by conventional techniques, and it is to be understood that the present invention is not limited to any particular techniques relating to these basic steps. However, for clarity and in order to bring out particular features of the invention, the drawing will be described with reference to preferred techniques for deasphalting, coking, and catalytic cracking.

A residual crude oil fraction is introduced to deasphalting zone 1 through line 2. This crude oil fraction will normally constitute the heaviest boiling fraction of a petroleum crude oil of the nature ordinarily employed as feed to a coking process. Thus, the residual oil may constitute the heaviest fraction of a crude oil derived by atmospheric and/or vacuum reduction of a crude oil, or other heavy hydrocarbons containing a substantial amount of constituents which cannot be vaporized without decomposition. Typically such feeds have an API gravity of about 0 to 20°, specifically, for example, 1.9° and a Conradson carbon content of about 5 to 50 weight percent, and specifically about 30%, for example. In this connection, the invention is of particular application to residual oils of relatively high Conradson carbon contents, and particularly in the range of about 10 to 40%. The deasphalting operation conducted in zone 1 may be carried out on a batch or continuous basis but is attractively conducted in the manner illustrated. Thus, deasphalting zone 1 may constitute a vertical tower into which the feed is brought at an intermediate point for contact with a deasphalting solvent introduced at the bottom of the tower through line 3. This deasphalting solvent may comprise low boiling hydrocarbons containing from about 2 to 5 carbon atoms in the molecule. Propane and butane are particularly desirable for use as

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a deasphalting solvent, although other low molecular weight hydrocarbons can be admixed with these. As will be developed, the deasphalting solvent can be obtained in the process to be described and may specifically constitute propane.

The deasphalting solvent passes upwardly through the tower countercurrent to the residual oil feed, permitting withdrawal of precipitated asphalt from the bottom of the tower through line 4 and a deasphalted oil from an upper portion of the tower through line 5. Contact of the solvent with the residual oil can be promoted by means of contacting plates, packing material, or the like in the tower. In general, the amount of solvent used per volume of oil may vary from about 4 to 10, preferably in the range from 6 to 8 volumes of solvent per volume of oil or specifically 6 volumes of solvent per volume of oil. Deasphalting is conducted at a temperature in the range of about 100 to 300° F., for example, at 160° F. As will be described, it is particularly desirable, although optional, to introduce deasphalting aids to the deasphalting zone through lines 6 and/or 7. These deasphalting aids constitute high boiling aromatic compounds, particularly characterized by containing a large number of condensed ring aromatic nuclei. Such compounds are of the nature of asphalt and will be precipitated by the deasphalting solvent. It has been found that presence of these compounds in the deasphalting zone causes a substantial increase in the elimination of metal contaminants from the deasphalted oil of line 5. Conduct of this deasphalting operation therefore provides a deasphalted oil in line 5, having a low or substantially zero Conradson carbon content and containing low amounts of metal contaminants. In addition, the deasphalting operation provides an asphalt product in line 4 having a higher Conradson carbon content and containing a higher concentration of metal contaminants than the oil feed to the deasphalting zone.

In accordance with this invention, the deasphalted oil of line 5 and the asphalt of line 4 are separately subjected to coking. This may be conducted in a blocked operation, using a single coking zone with alternate processing of these two coking feed stocks. Alternatively, and as illustrated, separate coking zones 8 and 9 may be employed.

The deasphalted oil stream of line 5 may be passed directly to the coking zone, or alternatively, deasphalting solvent may be stripped from the deasphalted oil for recycle to the deasphalting zone. Similarly, it is not necessary to subject the asphalt phase of line 4 to any processing prior to introduction to the coking zone.

Any desired type of coking may be carried out in zones 8 and 9. However, it is particularly preferred in the practice of this invention to conduct this coking employing a fluidized technique. A fluid coking process basically consists of a reaction vessel or coker and a heater or burner vessel. Heavy oil to be processed, in this case, constituting the deasphalted oil of line 5, or the asphalt of line 4, is injected into the reaction vessel containing a dense turbulent fluidized bed of hot inert solvent particles which are preferably coke particles. Steam is brought into the bottom of this bed so as to maintain fluidization. Uniform mixing in the fluidized bed results in substantially isothermal conditions and effects instantaneous distribution of the feed stock over the fluidized solid particles. The reaction zone is maintained at a temperature of about 900 to 1400° F., for example, 950° F., causing the feed stock to be partially vaporized, partially cracked, and partially coked. Product vapors are removed from coking zones 8 and 9 through lines 10 and 11, while coke remains in the bed, coated on the solid particles.

A stream of coke is transferred from the reactor to a burner vessel which may constitute a transfer line burner or a fluid bed burner, employing a standpipe and riser, air being supplied to the riser for conveying the solids

from the reactor to the burner. Sufficient coke or carbonaceous material is burned in the burning vessel by contact with fluidizing air so as to bring the temperature of the solids to a temperature sufficient to maintain the system in heat balance on transfer of the hot solids from the burner to the reactor. This is achieved by burning about 5% of the coke based on the feed. The net coke production which comprises the coke made in the coking reactor less the coke which is burned, may be withdrawn from coking systems 8 and 9 through lines 12 and 13 respectively. The coke of line 12 is of particular value by virtue of the fact that this coke is of low ash content.

The coking products of lines 10 and 11 are passed to similar fractionation systems 14 and 15. These fractionation systems 14 and 15 may constitute one or more stages of distillation, permitting segregation of the coker products into the desired distillate fractions. Thus, with reference to fractionation system 14, gases lighter boiling than propane may be withdrawn through line 16. A C_3 and/or C_4 hydrocarbon stream may be withdrawn through line 17. A naphtha stream boiling in the range of about 50 to 430° F. will be withdrawn through line 18 and a fraction boiling in the gas oil boiling range will be withdrawn through line 19. Finally, a residual oil fraction boiling above the end point of the gas oil fraction will be withdrawn through line 20. Similar fractions may be withdrawn from distillation system 15 through lines 21, 22, 23, 24 and 25.

As illustrated, at least a portion of the coker products including C_2 to C_5 hydrocarbons or the stream of line 17 (or line 22) may be recycled to the deasphalting zone 1 through line 3 for use as the deasphalting solvent. The residual oil portion of the coker products may be withdrawn from the system and used as desired, although generally these streams are recycled to coking zones 8 and 9 through lines 26 and 27 respectively. It is particularly desirable to pass a portion of these residual oil streams as, for example, through line 28, back to deasphalting zone 1. These streams contain high boiling aromatic compounds of the type earlier referred to which aid in eliminating metal contaminants from the deasphalted oil derived in the deasphalting zone 1. For this purpose, sufficient residual oil from fractionation system 14 may be passed back to the deasphalting zone through lines 26 and 28 so as to provide a concentration ranging up to about 25%, for example 5 to 25%, or about 20% based on the residual oil feed of line 2.

By virtue of the differences between the feed to coking zone 8 and coking zone 9, the gas oil of line 19 and the gas oil of line 24 will differ in nature. In particular, the gas oil of line 19 will have a lower Conradson carbon content and a substantially lower content of metal contaminants. As a result, it is practical to segregate a gas oil in line 19 having a boiling range of about 430° F. up to about 1150° F., or even higher, up to about 1300° F., having suitable characteristics for catalytic cracking. On the other hand, the gas oil segregated in line 24 will be fractionated in a narrower boiling range and particularly in the range of about 430° to 950° F., so as to have a suitably low content of metal contaminants for catalytic cracking. In this manner, as will be demonstrated, the ultimate yield of gas oil adaptable for catalytic cracking is maximized in the system described.

The gas oil streams of lines 19 and 24 are combined in line 30 for transfer to catalytic cracking zone 31. Any desired type of catalytic cracking may be carried out in zone 31 although preferably the cracking operation will constitute a fluidized cracking process.

The fluidized solids technique for cracking hydrocarbons comprises a reaction zone and a regeneration zone, employed in conjunction with a fractionation zone. The reactor and the catalyst regenerator are or may be arranged at approximately an even level. The operation of the reaction zone and the regeneration zone is preferably as follows:

An overflow is provided in the regeneration zone at the desired catalyst level. The catalyst overflows into a withdrawal line which preferably has the form of a U-shaped seal leg connecting the regeneration zone with the reaction zone. The feed stream introduced is usually preheated to a temperature in the range from about 500 to 650° F. by heat exchange with regenerator flue gases which are removed overhead from the regeneration zone, or with cracked products. The heated feed stream is then introduced into the reactor. Since there is no restriction in the overflow line from the regenerator, satisfactory catalyst flow will occur as long as the catalyst level in the reactor is slightly below the catalyst level in the regenerator when the vessels are maintained at about the same pressure. Spent catalyst from the reactor flows through a second U-shaped seal leg from the bottom of the reactor into the bottom of the regenerator. The rate of catalyst flow is controlled by injecting some of the air into the catalyst transfer line to the regenerator.

The pressure in the regenerator may be controlled at the desired level by a throttle valve in the overhead line from the regenerator. Thus, the pressure in the regenerator may be controlled at any desired level by a throttle valve which may be operated, if desired, by a differential pressure controller. If the pressure differential between the two vessels is maintained at a minimum, the seal legs will prevent gases from passing from one vessel into the other in the event that the catalyst flow in the legs should cease.

The reactor and the regenerator may be designed for high velocity operation involving linear superficial gas velocities of from about 2.5 to 4 feet per second. However, the superficial velocity of the upflowing gases may vary from about 1 to 5 feet per second and higher. Catalyst losses are minimized and substantially prevented in the reactor by the use of multiple stages of cyclone separators. The regeneration zone is also provided with cyclone separators. These cyclone separators usually include 2 to 3 or more stages.

Distributing grids may be employed in the reaction and regeneration zones. Operating temperatures and pressures may vary appreciably depending upon the products desired. Operating temperatures are, for example, in the range from about 800° to 1000° F., preferably about 850° to 950° F. in the reaction zone. Elevated pressures may be employed, but in general, pressures below 100 pounds per square inch gauge are utilized. Pressures generally in the range from 1 to 30 pounds per square inch gauge are preferred. Catalyst to oil ratios of about 3 to 10, preferably about 6 to 8 by weight, are used.

The catalytic material used in the fluidized catalytic cracking operation are conventional cracking catalysts. These catalysts are oxides of metals of groups II, III, IV and V of the periodic table. A preferred catalyst comprises silica-alumina wherein the weight percent of the alumina is in the range from about 5 to 20%. Another preferred catalyst comprises silica-magnesia where the weight percent of the magnesia is about 20 to 35%.

The size of the catalyst particles is usually below about 200 microns. Usually at least 50% of the catalyst has a size in the range from about 20 to 80 microns. Under these conditions, with the superficial velocities as given, a fluidized bed is maintained where, in the lower section of the reactor, a dense catalyst phase exists while in the upper area of the reactor a disperse phase exists.

The catalytically cracked products are removed from zone 31 through line 32 for introduction to a fractionation system 33. In zone 33, distillation can be conducted so as to permit withdrawal of gaseous products through line 34, naphtha through line 35, a light gas oil through line 36 and residual high boiling products through line 37. In the practice of this invention it is particularly desirable to segregate a heavy cycle oil in line 37 boiling above about 850° F. At least a portion of this stream is preferably recycled to the deasphalting zone through

line 6 for use as a deasphalting aid. Sufficient heavy cycle oil may be recycled in this manner to provide an amount of at least about 20% based on the residual oil feed of line 2. It is to be understood that this recycle through line 6 may be conducted alternately or in conjunction with the recycle through line 7, earlier described. As emphasized, introduction of either of the streams 6 and/or 7 to the deasphalting zone aids in eliminating metal contaminants from the deasphalted oil stream of line 5.

The particular advantages and utility of the process described will be understood from the following statement of the nature and quantity of products obtainable in this system. In this connection, reference is made to Figure 2 of the drawings, illustrating the effect of the Conradson carbon content of a coker feed stock on the gas composition resulting from coking. The data graphically illustrated in Figure 2 was obtained by coking a large number of residual oils having varying Conradson carbon contents falling along the entire range of values between 0 and 35 weight percent. Each of these coking feed stocks was processed in from 4 to 33 runs to provide a firm basis for the data shown in Figure 2. The products of these coking operations were analyzed for content of C₂ and C₃ unsaturated hydrocarbons, and this data is plotted in Figure 2 with respect to the Conradson carbon content of the feed stock. It will be observed from this data that the proportion of unsaturated compounds present in the C₃ fraction of coker products and present in the C₂ fraction of coker products appreciably varies in accordance with the Conradson carbon content of the feed. Thus, for example, in comparing the proportion of C₃ unsaturates in the C₃ cut, this proportion varies from about 54% for 35% Conradson carbon feed to above 70% for a 0 Conradson carbon feed. Furthermore, it will be observed that this variation is a non-linear function of the Conradson carbon feed stock. The significance of such data can be appreciated by reference to the following example drawn from data such as that illustrated:

Example 1

As a base example, consider the coking of 100 pounds of a residual oil having a Conradson carbon content of 20%. Coking of this oil at a temperature of 950° F. will result in the production of about 9.2% of gas consisting of propane and lighter gases. This gas will contain about 11.3% of ethylene or will contain 1.04 pounds of ethylene yield for the original feed of 100 pounds of residual oil.

Example 2

As compared to Example 1, by deasphalting the residual oil identified, about 66 pounds of asphalt may be obtained having a Conradson carbon content of 30 weight percent. 34 pounds of deasphalted oil will be obtained having a Conradson carbon value below 1 weight percent. Coking of the asphalt at a temperature of 950° F. will provide a yield of gas consisting of propane and lighter constituents amounting to 10.2% based on the asphalt feed. Of this gas, 10.0% will constitute ethylene providing an ethylene yield of 0.66 pound, resulting from coking of the asphalt. Similar coking of the deasphalted oil will provide a yield of 7.0% gas consisting of propane and lighter constituents. Of this gas, 23.4% will constitute ethylene, providing an ethylene production of 0.56 pound from coking of this oil. The sum total of ethylene, obtained from the separate coking of the asphalt and deasphalted oil segregated from the residual oil, will therefore amount to 1.22 pounds per 100 pounds of residual oil feed. Comparing this data with that of Example 1, it will be observed that an improved yield of ethylene is obtained amounting to 17%. This data therefore shows the substantial advantage obtainable by splitting a feed to a coking process into a low and high Conradson carbon fraction and separately coking these fractions. While the data particularly referred to has considered only

ethylene production, production of other unsaturates including propylene and higher boiling unsaturates follow these same principles and show the same advantage in the process of this invention.

Example 3

In order to show the basic feature of obtaining a deasphalted oil of low metals content, in comparative experiments, a residual oil was deasphalted in a conventional fashion with a mixture of propane and butane alone, and in the presence of 20% of a wash oil constituting high boiling aromatic hydrocarbons. The residual oil employed had a Conradson carbon content of 18.7 weight percent and contained 13 pounds per thousand barrels of nickel contaminants. Deasphalting this oil at a temperature of about 160° F., employing a solvent to oil ratio of about 3 to 5 provided a deasphalted oil yield of 49 volume percent. This deasphalted oil contained only 0.67 pound of nickel contaminants per thousand barrels of oil. This deasphalting operation therefore served to remove substantially 95% of the nickel contaminants. The deasphalted oil had a Conradson carbon content of only 4.43 weight percent.

In the comparative deasphalting operation employing 20% of the aromatic wash oil based on the residual oil charged, even better results were obtained. In this case the yield of deasphalted oil amounted to 54 volume percent and had a Conradson carbon content of only 4.06 weight percent and a nickel contaminant content of only 0.20 pound per thousand barrels. It will be observed from this data that deasphalting serves to substantially eliminate metal contaminants from deasphalted oil. The significance of such data is particularly brought out in the following example.

Example 4

A residual oil having a Conradson carbon content of 20 weight percent when coked at 950° F. for a vapor holding time of 15 seconds, provides the following product yields:

Coke	wt. percent	22
C ₃	do	9
C ₄	vol. percent	3
C ₅ /430	do	20.5
430/1015	do	56

Deasphalting of this residual oil can be conducted to produce a deasphalted oil in yields of 90 volume percent based on the residual oil feed. By virtue of the reduction in Conradson carbon content and metal contaminant content obtained as indicated in the preceding example, this deasphalted oil will have a Conradson carbon content of 16 and nickel contaminants will be reduced by more than 50%. The asphalt obtained in this deasphalting step will amount to 10 volume percent based on the residual oil feed and have a Conradson carbon content of about 45% and a nickel concentration about 5 times that of the residual oil feed. When the deasphalted oil identified is subjected to coking at 950° F., the following product yields are obtainable:

Ultimate Yields, Gas Oil Cut Point	On Deasphalted Oil		On Residual Oil, 60% @ 925° F.
	80% @ 925° F.	60% @ 925° F.	
Coke, wt. percent	17.5	17.5	15.5
C ₃ , wt. percent	9	7	6
C ₄ /430, wt. percent	24	19	17
Gas oil, vol. percent	60	67	60

Since the deasphalted oil contains less than 50% of the metal contaminants of the residual oil feed, the gas oil obtained in this coking operation, boiling in the same boiling range, will have less than 50% as great a concentration of metal contaminants. It is therefore possible to extend the end-point of the gas oil derived from coking

of the deasphalted oil to about 1100° F., of which about 60% of this gas oil boils below 925° F. As a result, the yield of gas oil obtainable as shown in the tabulated data is about 60 volume percent based on the residual oil feed.

When coking the asphalt obtained from the deasphalting of the residual oil, the following yields are obtainable:

Ultimate Yields	On Asphalt	On Residual Oil
Coke, wt. percent.....	50	6
C ₈ , wt. percent.....	11.5	1
C ₉ /430, vol. percent.....	20	2
430/1015, vol. percent.....	30	3

In this case, since the gas oil obtained will have a higher metals content, the end point will be selected at about 1015° F. or somewhat lower, in order to minimize the content of metal contaminants. However, it will be observed that the yield of gas oil obtainable from coking of the deasphalted oil and asphalt separately is about 63 volume percent based on the residual oil feed. This figure is comparable to the 56 volume percent yield obtainable on coking residual oil without the deasphalting step, demonstrating a yield advantage of about 12.5%. This data therefore shows the pronounced advantage of the process of this invention in terms of gas oil yields obtainable.

As described therefore, the process of this invention concerns the upgrading of residual oil to ultimate distillate products by employing a combination deasphalting and coking process. The invention has been described with particular reference to the deasphalting of a residual oil followed by separate coking of the deasphalted oil and asphalt obtained. As emphasized, this processing and this sequence is particularly desirable in maximizing yields of unsaturated hydrocarbons as well as increasing the amount of gas oil suitable for catalytic cracking. However, substantial advantages can also be obtained by the practice of this invention by first coking a residual oil followed by deasphalting of the gas oil product. In this case comparable advantages in terms of the amount of gas oil of suitable quality for catalytic cracking are achieved.

The process of this invention has also been described with particular reference to a fuels coking process employing a coking temperature in the range of about 800° to 1200° F. or preferably about 950° F. Conduct of such a coking process is particularly attractive in providing the greatest ultimate yields of distillate fuel products. Consequently, in this process the present invention permits obtaining increased yields of unsaturated hydrocarbons while at the same time providing maximum yields of distillate fuel products. However, the principles of this invention are also of particular value for higher temperature coking operations which further contribute to production of unsaturated hydrocarbons. In this connection the coking operation can be conducted at temperatures above 1200° F. ranging upwardly to about

1800° F., so as to further improve the yields of unsaturated hydrocarbons obtainable.

Another advantageous variation of this invention entails coking of deasphalted oil in the lower temperature range of about 800 to 1200° F., for example at 950° F., and coking of the asphalt obtained in the deasphalting operation at the higher temperature range of about 1200° to 1800° F. for example at 1600° F. This technique provides a valuable embodiment of the invention serving to attractively maximize both fuel and chemical production.

What is claimed is:

1. A residual oil conversion process which comprises the steps, in combination, of: separating a residual oil having a Conradson carbon content in the range of 5 to 50 wt. percent and a gravity in the range of 0 to 20° A.P.I. by deasphalting using a solvent comprising light hydrocarbons having 2 to 5 carbon atoms to obtain a solvent-containing deasphalted oil having a substantially lower Conradson carbon content and a solvent-containing asphalt; separately coking in two individual coking steps said solvent-containing deasphalted oil and solvent-containing asphalt by contact with fluidized solids at a temperature in the range of 900-1400° F., recovering from the deasphalted oil coking step a gas oil having an end point above 1100° F., separately recovering from the asphalt coking step a gas oil having an end point substantially below 1100° F.; combining and catalytically cracking the two gas oil streams having characteristically different end points which have been so recovered by contacting said gas oils in a catalytic cracking zone with fluidized cracking catalyst at a temperature in the range of 800 to 1000° F.; and recovering hydrocarbon products from the catalytic cracking zone effluent.
2. The process of claim 1 wherein a heavy cycle oil boiling above 850° F., amounting to at least 20 wt. percent on said residual oil, is recovered from said catalytic cracking zone effluent and recycled to the deasphalting step.
3. The process of claim 1 wherein propane is recovered from the products of said coking step and is recycled to the deasphalting step, constituting said solvent.
4. The process of claim 1 wherein the Conradson carbon content of said solvent-containing deasphalted oil is substantially zero.

References Cited in the file of this patent

UNITED STATES PATENTS

2,069,191	Atwell	Jan. 26, 1937
2,150,119	Heisig	Mar. 7, 1939
2,337,448	Carr	Dec. 21, 1943
2,528,586	Ford	Nov. 7, 1950
2,559,285	Douce	July 3, 1951
2,700,637	Knox	Jan. 25, 1955
2,727,853	Hennig	Dec. 20, 1955
2,738,307	Beckberger	Mar. 13, 1956
2,766,177	Buether et al.	Oct. 9, 1956
2,777,802	Peet	Jan. 15, 1957