CONVERSION OF ASPHALTIC HYDROCARBONS


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8 Claims. (CI. 196—53)

The present invention is directed to a process for producing valuable products. More particularly, the invention is directed to a process for producing valuable products from asphaltic hydrocarbons. In its more specific aspects, the invention is directed to the conversion of asphaltic hydrocarbons to hydrocarbons having a boiling range lower than the asphaltic hydrocarbons.

The present invention may be briefly described as involving the production of valuable products, such as gas oils, heating oils, and naphthas from asphaltic hydrocarbons in which a feed mixture of an asphaltic hydrocarbon and a diluent hydrocarbon is formed. The feed mixture is then contacted under reaction conditions with a desulfurization-cracking catalyst. The reaction conditions suitably include a temperature in the range between 725° and 825°F., hydrogen in an amount in the range between 500 and 6000 cubic feet per barrel of feed mixture, at a pressure in the range between 100 and 1000 pounds per square inch gauge and at a space velocity in the range of 0.25 to 5 volumes of mixture per volume of catalyst per hour. There is recovered from the contacted mixture the several valuable hydrocarbons of lower boiling range than the asphaltic hydrocarbons.

The diluent hydrocarbon employed in the practice of the present invention should contain a substantial amount of a cyclic hydrocarbon, such as naphthenes, and aromatic naphthenes, in liquid paraaffins and is also useful in the present invention. Catalytic cracking of cyclic hydrocarbons, such as naphthenes, and aromatic naphthenes, which contain both an aromatic and a naphthenic ring. The diluent hydrocarbon may suitably boil in the range between 120° and 1000°F. but preferably in the range between 430° and 650°F. and have a boiling range such that at least 30% by volume of the diluent hydrocarbon remains in the liquid phase under the reaction conditions. The boiling range of the diluent hydrocarbon is such that at least 50% by volume of the diluent hydrocarbon boils above 300°F. with not in excess of 50% by volume of the diluent hydrocarbon boiling above 850°F.

Examples of the diluent hydrocarbon feeds suitable in the practice of the present invention are heating oil fractions from crude oils from the Gulf Coast fields and the West Texas fields, sulfur dioxide extracts of Coastal heating oils, catalytic tars resulting from the thermal cracking of cyclic oils produced in catalytic cracking, heating oils produced in catalytic cracking operations and cycle stocks from catalytic cracking operations, or fractions of such various diluents obtained either by distillation, solvent precipitation, such as with propane or the like. These types of fractions should contain substantial amounts, which may range from 10% to 50% by volume of cyclic hydrocarbons, such as naphthenes, aromatics, and aromatic-naphthenes, which may contain both an aromatic and a naphthenic ring. For example, the Coastal heating oils are rich in aromatic-naphthenes and are quite satisfactory. West Texas heating oil is rich in sulfur compounds and also contains naphthenic hydrocarbons and is also useful in the present invention. Catalytic cracker of the nature described, as well as the sulfur dioxide extracts, heating oils and the cycle stocks formed in catalytic cracking operations, are rich in poly cyclic aromatic hydrocarbons which are useful in the present process. Thus we may select as our diluent any one of many hydrocarbon fractions provided the diluent hydrocarbon meets the requirement of boiling range and cyclic hydrocarbon content.

The diluent hydrocarbon may be used in admixture with the asphaltic hydrocarbon in an amount no less than about 0.5 part per part of asphaltic hydrocarbon. However, the diluent hydrocarbon may be used in an amount in the range between 0.5 and 3 parts of diluent per part of asphaltic hydrocarbon.

The asphaltic hydrocarbon forming a component of the feed mixture may be any asphalt-containing fraction. For example, it may be a crude petroleum, such as from the Hawkins Field, or asphaltic crude petroleum, such as obtained from the asphaltic crude fields in Mexico. The asphaltic hydrocarbon may be a residue resulting from distillation of crude petroleum such as a residual fraction from distillation of Parachute crude and the like. There are many crude residues available in the petroleum refinery which may be used in the practice of our invention. These are usually obtained from what is termed "non-lubricating oil crudes" and may contain from about 5% to about 30% of high boiling materials which find little direct use except for asphalt purposes or for blending in fuel oil for use as a fuel. Thus it is contemplated that we may employ in our invention any asphaltic fraction which may be a crude petroleum or a residue of a crude petroleum. Likewise, we may employ asphaltic materials precipitated in the propane treatment of a crude residue containing asphalt.

The temperatures employed in the practice of the present invention may suitably range from 725° to 825°F., but preferably in the range from 750° to 800°F. Pressures may range from 100 to 1000 pounds per square inch gauge with pressures in the range from 300 to 600 pounds per square inch gauge preferred. Space velocities may range from 0.25 to 5.0 volumes of feed per volume of catalyst per hour but preferably from 0.25 to 2 volumes of feed per volume of catalyst per hour.

Hydrogen employed in the practice of the present invention may be any hydrogen-containing mixture and may be employed in an amount in the range from 500 to 6000 cubic feet of hydrogen per barrel of feed mixture, a preferred amount of hydrogen being in the range from 500 to 2000 cubic feet of hydrogen per barrel.

The catalyst employed in the practice of the present invention may be any desulfurization catalyst or any desulfurization-cracking catalyst of which there are many on the market. Examples of these types of catalysts will include cobalt molybdate, preferably on a support such as alumina, nickel-tungsten sulfide, molybdenum sulfide and many other catalysts of this nature which are not deactivated by contact with sulfur containing materials. The cobalt molybdate catalyst is to be preferred. It is to be noted, however, that while we term the catalyst "cobalt molybdate" this catalyst actually may be mixtures of oxides of cobalt, molybdenum and a support such as alumina.

The present invention may be further illustrated by reference to the drawing in which the single figure is a flow diagram of a preferred mode.

Referring now to the drawing, numeral 11 designates a tank in which a feed mixture of asphaltic hydrocarbon and diluent may be accumulated. The feed mixture may be formed by introducing an asphaltic hydrocarbon,
which may be a crude residue, by way of line 12 containing pump 13 and controlled by valve 14 into tank 11 by way of line 15 in admixture with a diluent hydrocarbon of the type indicated from a source not shown which is introduced into the system by way of line 16 containing pump 17; line 16 is controlled by valve 18. Line 16 connects into line 15 which, in turn, is controlled by valve 19.

The feed mixture in tank 12 is withdrawn therefrom by line 20 controlled by valve 21 and is pumped by pump 22 into a reaction zone 23 which suitably contains a bed of a catalyst of the nature described which, for purposes of this description, may be assumed to be cobalt molybdate on alumina. On passing through line 20 there is added to the feed mixture by way of line 25 controlled by valve 26 a sufficient amount of hydrogen in the range given to allow the reaction to proceed as is desired. The feed mixture including hydrogen is heated to reaction temperatures by passage through a furnace 7 containing heating coil 8 which is supplied with heat from burners 9. The heated mixture discharges from coil 8 by line 20a into reaction zone 23.

On passage of the mixture of hydrogen and feed through the reaction zone 24, the asphaltic hydrocarbon and its partially converted cracking reaction to hydrocarbons of lower boiling range; such hydrocarbons produced in the process may include naphtha, heating oil and heavier hydrocarbons. The converted product discharges from reaction zone 23 by line 27 which leads into a separation zone 28 wherein a separation is made between the fixed gases containing unconverted asphaltic hydrocarbon and the converted product. The hydrogen and other fixed gases are withdrawn from zone 28 by line 29 and may be recycled to line 25 while the converted products issue from zone 28 by line 30 and discharge thereby into a distillation zone 31 which may be a sinter or a distillation tower or a plurality of fractional distillation towers. Distillation zone 31, while shown diagrammatically in the drawing, is intended to include all auxiliary equipment usually associated with the modern distillation tower. For example, the zone 31 will include cooling and condensing means, means for inducing reflux and internal vapor-liquid contact means, such as bell cap trays, packing and the like. Zone 31 is also provided with a heating means illustrated by a steam coil or equivalent heating means 32 for adjusting temperature and pressure. Zone 31 is also provided with line 33 for removal of fractions lighter than gasoline, line 34 for removal of gasoline and naphtha hydrocarbons, line 35 for withdrawal of heating oil fractions and line 36 controlled by valve 37 for withdrawal of catalytic cracking feed. Zone 31 is also provided with line 38 for discharging of heavier fractions.

Zone 31 may be operated in any number of different ways. For example, all of the light fractions may be taken off as one fraction including heating oil, gasoline and lighter materials, leaving the catalytic cracking feed and the heavier fractions to be withdrawn by line 38 with valve 37 being closed. If desired, the lighter components of the diluent fraction may be withdrawn by line 33 and the heavier fraction withdrawn by line 38 subjected to suitable deasphaltation and other treatments to recover cracking stock and the diluent. Either of the several fractions may be recycled to line 16, such as the fractions withdrawn by lines 35, 36 and 38 as desired.

It is desirable in the practice of the present invention to charge the feed mixture to the reaction zone 23 until the conversion to desirable products tends to decrease. When such happens, valve 21 may be closed and valves 14 and 19 also closed allowing the diluent hydrocarbon to be routed by line 16 directly into line 20 and thence into zone 23 over the catalyst bed 24 in admixture with hydrogen introduced by line 25 as desired. This operation allows the catalyst to be regenerated. The diluent feed is continued over the catalyst for a period of time ranging from 8 to 48 hours and thereafter the valve 19 is opened and valve 39 in line 16 is closed allowing the feed mixture on opening valve 21 in line 20 to be routed again to reaction zone 23. Of course, valve 14 in line 12 may be opened allowing the makeup of feed mixture in tank 11.

The present invention results in the production of useful products, such as naphthas, gasolines, heating oils and gas oils from asphaltic materials. The invention is dependent on a number of operating variables. For example, pressure is important since at low pressures for example, below 100 pounds per square inch gauge, operating temperatures must be kept high and the overall reaction rate tends to fall off. The amount of diluent volatilized from the catalyst increases and, with excessive volatilization of the diluent, coking of the catalyst takes place. Operating at higher pressure but below 1000 pounds per square inch gauge allows the overall reaction toward desirable products to be increased since operating temperatures in the range given may be increased. In general, higher temperature results in increasing the ratio of gasoline to gas oil in the product. If pressures above 1000 pounds per square inch gauge are employed, gas production increases and hydrogen consumption therefore increases.

The diluent is also important in that the diluent serves to maintain a liquid phase on the catalyst. The boiling range of the diluent as indicated should be carefully selected; likewise, the content of aromatics and naphthenes. The naphthenes and aromatics serve as hydrogen donors and hydrogen acceptor donors, respectively. The aromatic materials are believed to exert a solvent or washing action on the catalyst to keep it in a clean non-coked condition.

An important feature of the present invention is the selection of the diluent as the feed stock composition. Thus asphalt alone may not be converted directly because of its high viscosity and because of coking reactions which take place. Over the temperature range of 725° to 825°F. employed in the present invention and at pressures which may range from 100 to 1000 pounds per square inch gauge and at moderate hydrogen rates of 500 to 6000 cubic feet per barrel of feed but preferably 500 to 1500 cubic feet per barrel of feed for selectivity reasons, only a few diluent hydrocarbons may be used successfully in diluting a predominately asphaltic feed. A light naphtha, such as a hydroformer feed stock containing aromatics and boiling from 200°F. to 350°F., may be used only at the higher pressures and low hydrogen rates in the range given since under the lower pressures and higher hydrogen rates in the rates given such diluent is almost completely vaporized under the conditions of the operation and, therefore, would not serve to eliminate the undesirable features of the prior art. The diluent may not be too heavy or too viscous since it has been observed that unless crude residua and other asphaltic materials are diluted with a suitable diluent the degree of conversion of the asphalt is substantially reduced. Thus in one run a crude residuum was diluted in a weight ratio of 40-60 with a heating oil and charged over a catalyst of the type disclosed at 400 pounds per square inch gauge, 760°F., 0.25 volumes of feed per volume of catalyst per hour, 1200 cubic feet of hydrogen per barrel to maintain a net conversion of asphalt of only 33%. On the other hand, a conversion of asphalt of 57% was obtained when passing a 40-60 weight ratio asphalt-heating oil blend over the same catalyst at 0.24 volumes of feed per volume of catalyst per hour, 600 cubic feet per hour and 1300 cubic feet of hydrogen per square inch gauge pressure and 760°F. The asphalt used in this run was obtained by propane precipitation from another portion of the same crude residuum used in the run noted just previously. These runs show that the heating oil boiling range material is an excel-
lent diluent and is to be preferred to heavy oils and light naphthas.

The temperatures to be employed in the present invention are dependent on vaporization and coking tendencies and also the degree of reaction to be obtained. Thus in a run at 700° F. the gravity of the product was substantially the same as the gravity of the feed. On the other hand, runs at higher temperatures, such as 790° and above, have indicated that temperatures not greatly in excess of 800° F. are to be desired, especially for non-regenerative operations. In regenerative operations, such as the type described herein, it is possible to operate at the higher temperatures in the range given. Thus the process was operated without severe coking at 765° F. over the range of 1000 to 6000 cubic feet of hydrogen per barrel of feed mixture. At 790° F. no difficulties were obtained with coking at 1000 to 5000 cubic feet of hydrogen per barrel. Other runs with a different cobalt molybdate on alumina catalyst indicated successful operation at 790° F. with 6000 cubic feet of hydrogen per barrel, but coking was experienced at 815° F.

During the course of operation the catalyst will tend to lose its ability to convert the asphaltic material to desirable hydrocarbons. It may suitably be regenerated by cutting out the asphaltic component of the feed mixture, charging only diluent to the catalyst bed in the presence of hydrogen at reaction conditions. The period of charging the diluents in the absence of asphalt may range from about 8 to 48 hours, sufficient to recon- dition the catalyst for conversion of asphalts to desirable hydrocarbons. After repeated reconditioning of the catalyst with diluent hydrocarbon it may become neces- sary to subject the catalyst to more severe regenerating conditions such as for example treatment with an oxygen-containing gas to burn off coke-like deposits which were not removed by reconditioning the catalyst with diluent hydrocarbon. The conventional procedures for oxidative regeneration may be used which will include the steps of displacing hydrocarbons from the catalyst zone such as by purging with an inert gas followed by control- lored addition of oxygen-containing gas to the zone either alone or in admixture with inert gas, such as flue gases.

In practicing the present invention, it is desirable that the catalyst be employed of a particular size. While pills of a certain size may give desirable results, it has been observed that reducing the size of the catalyst will give substantially increased conversion. For example, in one operation where a temperature of 760° F. was employed at a space velocity of feed of 0.24 volumes per hour of feed per volume of catalyst per hour, 1307 cubic feet of hydrogen per barrel, 400 pounds per square inch gauge with 1/4 inch pills of cobalt molybdate on alumina, the conversion was 57%. Under substantially identical con- ditions using 10 to 20 mesh activated cobalt molybdate on alumina the conversion was 63%.

The present invention results in the reduction in the Conradson Carbon of the asphaltic feed component. In several runs, Conradson Carbon reductions of 24, 5, 21 and 12%, respectively, were obtained or an average of about 15%.

In practicing the present invention it appears that in the regeneration, where the diluent feed replaces the feed mixture, the diluent feed serves to wash the catalyst at an elevated temperature. It is believed that this washing action serves to remove significant portions of the iron, nickel, vanadium and sodium as well as asphaltic hydro- carbons from the catalyst which may have been selectively adsorbed from the asphaltic feed.

Hydrogen rate in the present invention is critical from an operability standpoint and from the standpoint of results. In one run, nitrogen was substituted for hydrogen with the result that conversion immediately dropped off. When hydrogen within the range stated was recharged to the system, conversion became high but never did attain original values, indicating that coking or fouling of the catalyst had occurred during the period when nitrogen was charged. After the catalyst had been regenerated as has been disclosed, it was restored to at least its charge activ- ity. In a run at 765° F., 0.5 volume of feed mixture per volume of catalyst per hour, at 40 pounds per square inch gauge, 1000 cubic feet of hydrogen per barrel as compared with a run under similar conditions at a higher hydrogen rate of 6000 cubic feet per barrel which is the maximum limit of the range, it is shown that the desul- furization of the asphalt was much better at the lower hydrogen rate than at the higher hydrogen rate. For example, the weight percent of the sulfur in the product at the higher hydrogen rate was 1% against 0.77% at the lower hydrogen rate.

The employment of the desulfurization or desulfuriza- tion-cracking catalyst is also essential to the practice of the present invention. When attempts were made to oper- ate without a catalyst it was found that a degree of desul- furization of the product was much lower and lower con- versions were obtained under the same conditions than when catalysts were present. Also when it was attempted to improve the non-catalyst conversion by raising temper- atures, coking occurred.

The present invention contemplates a process in which a diluent hydrocarbon of the type mentioned will be em- ployed in a sufficient amount such that a substantial amount of diluent remains in the liquid phase on the catalyst while the feed mixture passes over the catalyst. This prevents coking of the catalyst and allows the desul- furization and cracking of the asphaltic material to desir- able fractions.

Furthermore, the present invention involves regenera- tion with the diluent liquid passing over the catalyst to remove undesirable adsorbed materials and also to recon- dition the catalyst for re-use in the process.

The nature and objects of the present invention having been completely described and illustrated, what we wish to claim as new and useful and to secure by Letters Patent is:

1. A process for producing lower boiling hydrocarbon products which comprises forming a mixture of an asphaltic hydrocarbon and an amount of a diluent hydrocarbon containing a substantial amount of cyclic aromatic and
naphthenic hydrocarbons in the range from 0.5 to 3 parts of diluent hydrocarbon per part of asphaltic hydrocarbon, said diluent hydrocarbon boiling in the range between 200° and 1000° F., contacting said mixture with a supported catalyst comprising oxides of cobalt and molybdenum under reaction conditions including a temperature in the range between 725° and 825° F. in the presence of hydrogen in an amount in the range between 500 and 6000 cubic feet per barrel of mixture at a pressure of 100 to 1000 pounds per square inch gauge and at a space velocity of 0.25 to 5 volumes of mixture per volume of catalyst per hour, and recovering from said contacted mixture valuable hydrocarbons of lower boiling range than the asphaltic hydrocarbons, at least 30% by volume of said diluent hydrocarbon remaining in the liquid phase under said reaction conditions and at least 50% by volume of diluent hydrocarbon boiling above 300° F. with not in excess of 50% by volume of diluent hydrocarbon boiling above 850° F.

6. A process in accordance with claim 5 in which the diluent is a West Texas heating oil.

7. A process in accordance with claim 5 in which the diluent is a hydrocarbon fraction rich in polycyclic aromatic hydrocarbons.

8. A process for producing lower boiling hydrocarbon products which comprises forming a feed mixture of an asphaltic hydrocarbon with from about 0.5 to 3 parts per part of asphaltic hydrocarbon of a diluent boiling in the range between 430° and 650° F. and containing a substantial amount of aromatic and naphthenic hydrocarbons, contacting said feed mixture with a supported catalyst comprising oxides of cobalt and molybdenum under reaction conditions including a temperature in the range between about 750° and 800° F. in the presence of hydrogen in an amount between 500 and 2000 cubic feet of hydrogen per barrel of feed mixture at a pressure of about 300 to 600 pounds per square inch gauge and at a space velocity of 0.25 to 2 volumes of feed per volume of catalyst per hour, and recovering from said contacted mixture valuable hydrocarbons of lower boiling range than the asphaltic hydrocarbon, at least 30% by volume of said diluent remaining in the liquid phase under said reaction conditions and at least 50% by volume of the diluent boiling above 300° F. with not in excess of 50% by volume of the diluent boiling above 850° F.

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