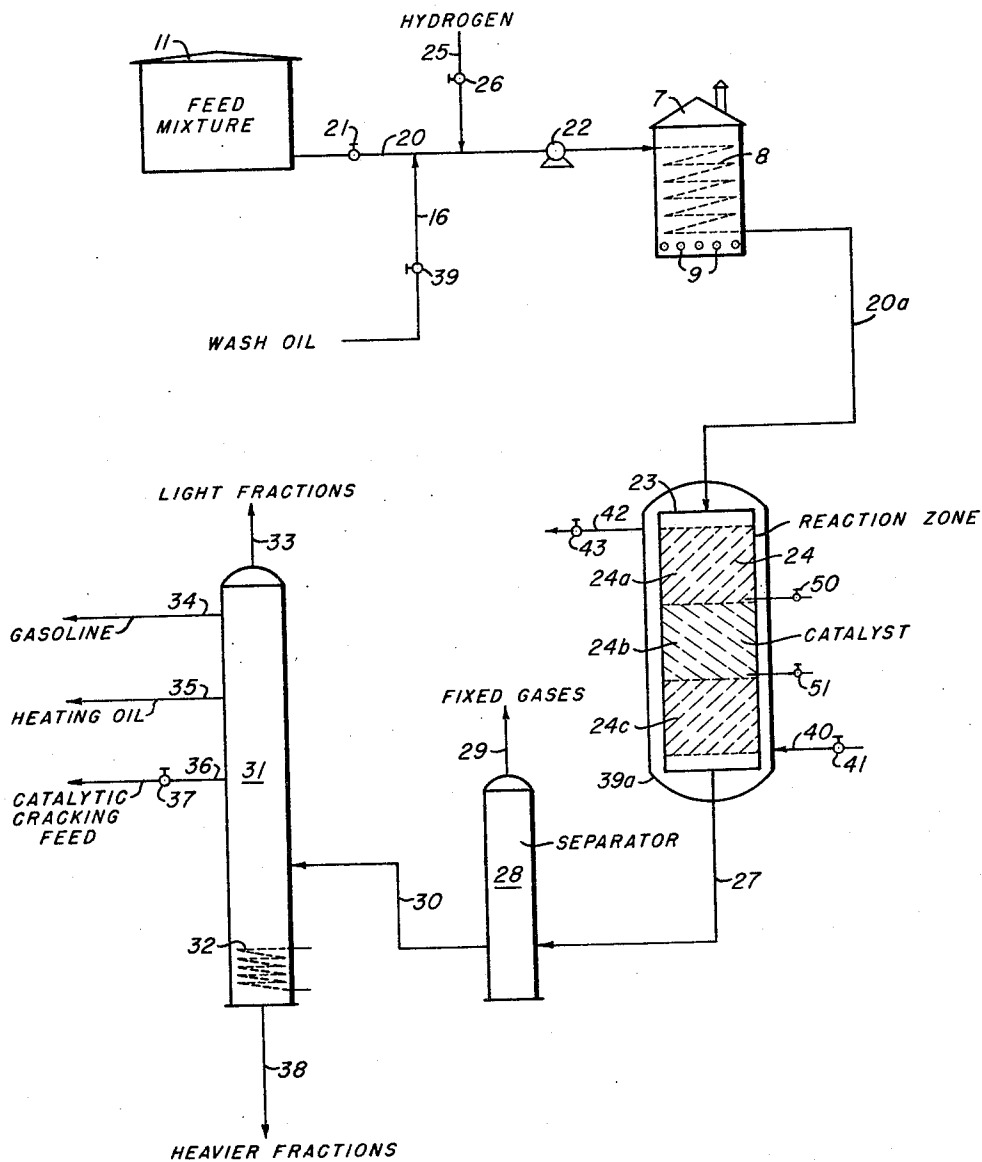


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CONVERSION OF ASPHALTIC MATERIALS

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CONVERSION OF ASPHALTIC MATERIALS

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The present invention is directed to an improved process for producing valuable products from asphaltic-type materials. More particularly, the invention is directed to a process for the catalytic conversion of asphaltic materials in the presence of porous catalysts.

One aspect of the present invention may be briefly described as contacting an asphaltic material with a catalyst under asphalt conversion conditions whereby one or more properties of the asphaltic material are improved. In a particularly preferred embodiment, asphaltic material essentially free of normally liquid diluents is converted in the presence of hydrogen to useful lower boiling materials under conditions adapted to give long catalyst life.

It is well known in the prior art to conduct conversion operations on asphaltic materials for the purposes of producing conversion products by hydrogenating, desulfurizing and cracking and for improving various characteristics of the asphalt. The prior art processes have suffered from various limitations, particularly from the standpoint of the tendency to degrade the catalyst rapidly at the high operating temperatures needed to obtain substantial conversions. In addition, low space velocities, i.e., relatively long contact times, have been required with conventional catalysts to obtain a desired degree of conversion. Furthermore, all processes which have even approached, commercial utility have required very high operating pressures, in the range from 1500 to 5000 p.s.i.g. or even higher.

It is also frequently an advantage to treat sulfur-containing asphaltic materials, such as those produced from crude petroleum oils, in the presence of hydrogen to form low sulfur products useful for blending with lower boiling hydrocarbons in order to make fuel oils. Because of the tendency of the asphaltic material to be degraded during the conversion process to form large amounts of naphtha insoluble materials in the product, the amount of such treated asphalts that could be blended with lower hydrocarbons has met with definite limitations.

It is a principal object of the present invention to minimize the shortcomings of the prior art processes and to maximize the yield and quality of useful products that can be obtained from asphaltic materials in catalytic conversion operations carried out at a given set of conditions.

A special feature of the present invention is based on a critical relationship of the hardness of the asphalt fraction being treated and the maximum temperature permissible in the zone in which such asphalt fraction is being treated in a low pressure operation. It has been found that the maximum temperature permissible in a reaction zone in which hard asphalt is being treated may be defined by the equation

$$T = [825 - 6(I - 5)] \pm 25$$

wherein T is the maximum reactor temperature in ° F. and I is the percent insoluble in naphtha plus five percent CS₂, determined by the test described below, of that fraction of the feed stock which boils above 900° F. The correlation is based on the finding that the result of said test on the 900° F. and higher boiling feed fraction is a good indication of the hardness of the asphalt, and that the maximum temperature permissible in the reaction

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zone may be directly related to the asphalt hardness in this manner.

It will be seen that the foregoing equation defines "T" as a temperature range rather than a single temperature point. Operation of a reactor at the lower end of the range T permits long continued operation of a reactor without any apparent catalyst deterioration. Operation near the middle of range T still permits runs of reasonable length, but gradual catalyst deterioration will take place, particularly due to coking of the catalyst. The upper limit of the range may not be substantially exceeded without experiencing severe and rapid catalyst deterioration. Pressure and hydrogen ratio also influence catalyst life. Thus, at lower pressure and higher hydrogen to oil ratio within the limits defined, a higher temperature in the stated range may be employed.

The "percent insoluble in naphtha plus 5 percent CS₂" is referred to herein, for convenience, as "naphtha insolubles." It may be determined as follows:

(1) 1.0±0.1 gram of the sample to be tested is weighed to the nearest milligram in a clean, dry, tared, 125 ml. glass stoppered Erlenmeyer flask.

(2) Exactly 5 ml. of chemically pure carbon bisulfide is added to the flask. The flask is whirled a number of times to dissolve the sample as completely as possible.

(3) Exactly 100 ml. of 86° naphtha is added to the flask.

86° naphtha is defined as follows: It is cut from a paraffin base crude. It has a gravity in the range from 86° to 88° API. In an Engler distillation, not less than 10% thereof distills over between 95° and 150° F. The aniline point of the naphtha is between 152 and 156 when calculated from the aniline point test on a blend of 35% naphtha and 60% normal heptane.

(4) The stopper is placed in the flask and the latter, with its contents, is shaken vigorously for one minute.

(5) The flask is placed in a water bath such that the water level in the bath is above the liquid level in the flask. The flask remains in the bath for at least two hours at 100°±1° F.

(6) The flask is removed from the water bath and the contents immediately filtered through a tared Gooch crucible. Suction is applied gently at first and is then increased to a pressure of 20 inches of mercury in the filtering flask. Care must be taken to prevent loss of sample during filtration.

(7) The flask and stopper are washed with two 50 ml. portions of 86° naphtha and the washings filtered through the tared crucible.

(8) The crucible, flask and stopper are dried for one hour in an air oven at 221° F., cooled in a desiccator, and weighed to the nearest milligram.

(9) The increase in weight of crucible, flask and stopper represents the total amount insoluble in the naphtha plus CS₂. This is reported as percent of the original sample.

(10) It is preferred to make the test in duplicate, and use the resulting average value, provided the individual results do not differ from the mean by more than 5 percent of the mean. If the individual results do differ by more than 5% of the mean, two additional tests should be made, the least concordant result discarded, and the remaining three averaged.

The naphtha insolubles content of a residual stock is believed to represent substantially the content of asphaltenes in the fraction tested.

In accordance with another feature of this invention, it has also been found that concentrated asphaltic materials; i.e. asphalts substantially free of diluting lower boiling hydrocarbons, may be converted to useful lower boiling hydrocarbons and improved asphalts in a low

pressure multi-stage operation conducted in the presence of hydrogen and a hydrocracking catalyst without rapid catalyst degradation. The concentrated asphalt contacts the catalyst in a first zone operated at below 1000 p.s.i.g. and at a hydrocracking temperature that is below the incipient coking temperature of the asphalt at the feed rate used, as determined by Equation 2, *supra*. Substantial amounts of diluting lower boiling hydrocarbons are formed in this first zone. The total effluent from the first zone passes to a second catalyst zone operated at a higher temperature than the first, but below the incipient coking temperature of the effluent feed thereto, also determined by Equation 2, to obtain still further conversion. Additional higher temperature zones may be used after the second zone, provided the total effluent from each previous zone is charged to the adjacent zone. This operation permits long catalyst life between regenerations. It also avoids the need for extraneous diluting hydrocarbons in the original feed, since such diluents increase reactor space and recovery equipment requirements and frequently lead to increase in naphtha insolubles in the product.

The preferred catalyst of the present invention comprises a porous base material having impregnated therein an active metal-containing catalytic component. A variety of metals, mixtures of metals, metal compounds or mixtures of metal compounds may be used as active catalyst components on the porous base. For example, suitable metallic agents may be chosen from the group of metal oxides, halides, sulfides, selenides, phosphates, manganates, molybdates, chromates and the like. Metals of group VI of the periodic table are especially useful. A preferred class of catalysts to be utilized in accordance with the present invention are catalysts having pore characteristics inter-related with the average diameter of the feed stock as disclosed, for example, in co-pending application Serial No. 490,732, now Patent No. 2,890,162, entitled "Improved Porous Contacting Agents and Use Thereof," filed on an even date herewith in the names of James A. Dinwiddie, Max A. Mosesman, James A. Anderson, Jr., and Lonnie W. Vernon, the disclosures of which are made a part hereof.

Although the invention is not restricted to the use of any particular catalyst containing any specific amount of an active metal or metal compound, it is generally preferred to use active metal-containing components that are not impaired by the sulfur compounds so frequently present in asphaltic materials. For this reason, compounds of molybdenum, tungsten, nickel, iron cobalt and other sulfur insensitive metal components are usually preferred. Molybdena, cobalt molybdate or mixtures of cobalt and molybdena form particularly preferred catalytic agents.

In general, the porous support will be in gravimetric excess of the active metal or metal compound, and good results may be obtained by employing compound catalyst containing from about 0.1% to about 40% by weight of the active material. A more suitable concentration range is generally from about 0.5 to about 20% by weight of the catalyst mass.

The porous support employed in the practice of the present invention may be prepared from one or more of the well-known porous solids, such as alumina, charcoals and the like, but alumina constitutes the preferred material because of its relatively high activity as a base material.

The asphaltic materials useful in the present invention include bitumen, asphaltic residua obtained by vacuum distillation of crude petroleum oils, asphalts obtained by conventional solvent deasphalting of crude residua, tarry substances obtained in the oxidation of high molecular weight hydrocarbons, asphalts obtained from hydrogenated coal products, and the like. These feed stocks may include substantially non-asphaltic hydrocarbon components, such as high molecular weight resinous hydro-

carbons, and other high boiling hydrocarbons, but will usually contain above about 15 to 20% of asphaltic substances. The feed stocks of the present invention will boil substantially completely above 900° F.

The above-described catalysts find particular application in converting concentrated asphaltic materials that are substantially free of lower boiling and non-asphaltic hydrocarbons. These asphaltic materials will generally have less than about 15% of materials boiling below 1050° F. and are characterized by relatively high Conradson carbon contents, substantial amounts of sulfur compounds and frequently contain relatively large amounts of metal compounds. They are also characterized by being semi-solid or solid materials with relatively high viscosities and/or softening points and relatively high naphtha insolubles contents, such as above 5 weight percent.

In carrying out a conversion process, a variety of reactions may be secured depending on the type of catalyst employed and the conditions to which the asphalt is subjected. Such reactions include desulfurization, cracking, hydrocracking, hydrogenation, and the like. It is frequently desirable, for example, to crack the asphalt in the presence of hydrogen to form valuable lower boiling hydrocarbons but at the same time to remove substantial amounts of sulfur. Such reactions may be carried out with the catalyst in various forms and in reaction zones employing a fixed catalyst bed, moving beds of catalyst, catalyst suspended in the reactants, etc. The invention has particular reference, however, to operations employing the catalyst in the form of a fixed bed in which the catalyst particles range in size from about 20-40 mesh up to as high as 1/4" x 1/4" or even larger size pills.

It is particularly preferred to carry out the operation in the presence of hydrogen or a hydrogen-containing gas in order to reduce the tendency of the catalyst to be degraded by the formation of carbonaceous deposits, to hydrogenate the asphalt, and to aid in the desulfurization thereof.

The temperatures employed in the practice of the present invention may suitably range from 650° to 825° F. or higher but generally asphalts coke badly at the higher temperatures, and those from about 700° to 800° F. are preferred. In operations with concentrated asphalts in multi-stage operations, initial temperatures of below 750° F., such as from 650° to 730° F. are most useful, with temperatures in subsequent stages being increased by increments of 5° to 10° F. or more. The maximum permissible temperature in each reaction zone is determined by use of Equation 2, *supra*.

Pressures ranging from 100 to 5000 pounds per square inch gauge or higher may be used. Pressures below 1000 p.s.i.g., and in the range from 200 to 900 p.s.i.g., are preferred.

Space velocities may range from 0.25 to 5.0 volumes of feed per volume of catalyst per hour but preferably are in the range 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 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 an asphaltic material may be accumulated. The feed in tank 11 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 24 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

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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 temperature by passage through a furnace 7 containing a heating coil 8 which is supplied with heat from burners 9, the maximum permissible temperature is selected in the range determined from Equation 2. 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 23, the asphaltic hydrocarbons are substantially converted in a desulfurization-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 unconsumed hydrogen 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 single 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 adjustments of 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 may be withdrawn by line 36 and the heavier fraction withdrawn by line 38 subjected to suitable deasphalting and other treatments to recover cracking stock.

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 decreases. When such happens, valve 21 may be closed allowing a wash oil, such as gas oil, to be routed by line 16 containing valve 39 directly into line 20 and thence into the 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 wash oil is continued over the catalyst for a period of time ranging from 8 to 48 hours and thereafter 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.

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 low and the overall reaction rate tends to fall off and coking of the catalyst takes place. Operating at higher pressure allows the overall reaction toward desirable products to be increased since operating temperatures in the range given may be

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increased. In general, higher temperature results in increasing the ratio of gasoline to gas oil in the product. It is usually less preferred to operate at pressures above 1000 pounds per square inch gauge since gas production and hydrogen consumption frequently increase to undesirably high levels.

After repeated reconditioning of the catalyst with wash oil it may become necessary 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 wash oil. 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 controlled addition of oxygen-containing gas to the zone either alone or in admixture with inert gas, such as flue gas.

In a preferred embodiment of the invention particularly when treating concentrated asphalts that have relatively high softening points such as above about 175° F., it is preferred to operate with an increasing temperature gradient through the reaction zone or to conduct the operation in a plurality of reaction zones connected in series whereby the temperature in each subsequent zone may be increased. This type of operation has been found to be particularly advantageous for reducing the tendency of the feed to foul the catalyst during the initial reactions, after which the severity of the treating conditions may be increased without substantial fouling of the catalyst. One method is shown in the drawing in which reactor 23 is provided with a jacket 39A containing a lower inlet line 40 controlled by valve 41 and an upper outlet line 42 controlled by valve 43. A suitable heating fluid, such as heated flue gas, is charged into the reactor jacket via line 40 and withdrawn through line 42 under conditions such that portions 24a, 24b and 24c of the catalyst bed are maintained at successively higher temperatures.

For example, let the feed in charge tank 11 be an asphalt boiling above 900° F. whose naphtha insolubles content I is determined to be 20. Then, from Equation 2, $T = [825 - 6(20 - 5)] \pm 25$, or $T = 735 \pm 25^\circ$. For maximum catalyst life, the operating temperature may be chosen at 710° F., the lowest defined temperature. During startup, temperatures of about 710° F. are maintained throughout the reactor. Samples are withdrawn from sampling points 50 and 51, located at the exit of reactor sections 24a and 24b, respectively. The naphtha insolubles content I of these samples is determined as described supra. The values may be found to be 17 and 14. Permissible temperatures for reactor sections 24b and 24a are calculated from these values, by Equation 2, to be

$$T \text{ (for section 24b)} = 753^\circ \text{ F.} \pm 25^\circ$$

and

$$T \text{ (for section 24c)} = 771^\circ \text{ F.} \pm 25^\circ$$

The jacket temperatures may then be adjusted to raise temperatures of sections 24b and 24c to at least the lowest defined temperatures, namely 728° F. and 746° F., respectively. After these conditions are established another set of samples may be taken from sampling points 50 and 51. The naphtha insolubles content I of these samples may be found to be 15 and 12, respectively, due to the more severe operation. Permissible temperature ranges may again be calculated, and will be found to be $765^\circ \text{ F.} \pm 25^\circ$ and $773^\circ \text{ F.} \pm 25^\circ$, for beds 24b and 24c, respectively. The jacket temperatures may be adjusted upward accordingly. It will be evident to the person skilled in the art that the maximum permissible temperature gradient may be established more quickly and simply than described above by employing during startup a gradient in the range from 710° to 760°, the range defined by applying Equation 2 to the feed in tank 11.

It will be seen that during passage of the feed through

the reactor, the naphtha insoluble content is substantially decreased. This permits operation at higher temperatures in the downstream portions of the reactor, as described, thus increasing asphalt conversion without causing rapid deterioration of the catalyst.

Another method for increasing temperature gradient is that of injecting heated hydrogen into the reaction zone at spaced points along the reactor axis, the temperature of the hydrogen streams being individually adjusted to give the desired temperature increase in the direction of flow of the feed.

Other modifications will include employing two or more separate reaction zones connected in series with appropriate heating means positioned between any two adjacent reaction zones whereby the temperature of the effluent from one zone may be increased to the appropriate range for introduction into the next adjacent zone. The temperature gradient employed between adjacent zones will vary depending on the characteristics of the asphalt, but generally will be above about 5° F. and below about 50° F., preferably from about 10° to 20° F., increase from zone to zone.

The invention will be described in more detail in conjunction with the following examples:

EXAMPLE 1

Mild hydrogenation-desulfurization runs were carried out on two concentrated asphalt feed stocks in a fixed bed treating unit. The reactor was provided with an inlet which introduced preheated asphalt and preheated hydrogen, along with suitable product take-off equipment. Conventional means including suitable pumps, flow meters, and the like were provided for maintaining the desired operating pressure, feed rates and the like.

Asphalt No. 1, used in runs 1-3, was produced in 41 volume percent yield from a composition of nonlube residuum obtained from Coastal, Hawkins, West Texas, Salt Flat, and mixed sweet crude oils. This residuum blend was deasphalted with 3 volumes of propane-butane solvent at 385 p.s.i.g. and pressure and an average temperature of about 170° F.

Asphalt No. 2 used in runs 4-6 was produced in a 52 volume percent yield from a vacuum West Texas residuum which represented 13.9 volume percent residuum based on the crude oil. The residuum was deasphalted with 3 volumes of propane-butane solvent at 400 p.s.i.g. and an average temperature of about 170° F. The asphalt had an average molecular diameter of about 74 Å.

The catalyst used in the runs consisted of 15% CoMoO₄ on granular low silica, gamma alumina, prepared in the following manner:

A commercial-type cobalt molybdate catalyst supported on granular gamma alumina, containing 15 weight percent cobalt molybdate, in the form of $\frac{3}{16}$ inch pills was heat treated for 24 hours at 1400° F. in the presence of dry moving air. The heated product was then given a further heat treatment for 24 hours at 1500° F., crushed and screened to form a 10 to 20 mesh material which was used as the catalyst. This catalyst had a surface area of 72 m.² per gram, a pore volume (based on the hysteresis loop) of 0.201 ml. per gram, a D_r of 90 Å, a ΔD_r of 30 Å. and a pore size-distribution factor of 24.

In conducting runs 1-3 on asphalt No. 1, the unfluxed asphalt in the presence of hydrogen was passed through fresh catalyst in three reactors operating in series at successively higher temperatures. The reactor temperature was separately controlled in three sections of the reactor and was separately measured near the inlet, the middle, and the outlet. A portion of the product from each reactor was withdrawn and evaluated, the remainder of the total product from run 1 being charged to run 2, and that from run 2 to run 3, each at the higher temperature. Fresh portions of catalyst were employed for each run.

The reaction conditions for the three runs are shown at Table I below:

Table I

Run No.	1	2	3
Pressure, p.s.i.g.	800	800	800
Range of reactor temperature, ° F.	699-750	688-749	730-765
Range of average reactor temperatures, ° F.	715-730	720-740	745-755
Liquid space velocity, v./hr./v.	1.74	1.77	1.73
Hydrogen, SCF/bbl. feed	1,130	2,190	2,360
Run length, hours	83	40	17

Similar runs were carried out on asphalt No. 2, labeled as runs 4-6. In runs 4 and 5, fresh catalyst was used in the reaction zone during each run. In run 6 the catalyst was the same as that used in run 5, however, the catalyst from run 5 was washed with a gas oil before charging the product from run 5 thereto. Operating data for runs 4-6 are shown in Table II below:

Table II

Run No.	4	5	6
Pressure, p.s.i.g.	800	800	800
Range of reactor temperature, ° F.	690-740	720-745	725-761
Range of average reactor temperatures, ° F.	710-725	730	740-750
Liquid space velocity, v./hr./v.	1.82	1.78	1.91
Hydrogen, SCF/bbl. feed	2,220	2,300	2,150
Run length, hours	51	38	21

After run 6 was finished, asphalt 2 was charged to the same catalyst under run 4 conditions, and there was no indication of catalyst activity decline after 140 hours of operation.

Inspections on the feed stocks and products for runs 1-6 are shown in Table III.

All the above runs were voluntarily terminated. Indications were that in run 1 some coking of the catalyst had occurred in a section of the catalyst bed during a 12 hour period in which that section was maintained at 750° F. At all other conditions described the catalyst retained full activity and remained substantially clean.

Table II-A, below, shows the actual reactor temperatures and the values for temperatures T, calculated from the equation for the runs 1-6, rounded off to the nearest whole number.

Table II-A

Run No.	1	2	3	4	5	6
T, ° F.	728-773	740-790	754-804	756-806	778-828	787-837
Range of reactor temperature, ° F.	699-750	688-749	730-765	690-740	720-745	725-761

It will be seen that in run No. 1, the highest actual temperature, 750°, was almost exactly in the middle of the range defined by T, the middle being 753° F. As stated above, there were indications that during 12 hours at that temperature, some coking of the catalyst bed occurred. In runs 2 and 3, the highest actual temperature was only about 10° F. above the lowest temperature T, and no difficulty was observed in runs of 40 and 17 hours, respectively. In runs 4, 5 and 6, the conditions employed were milder than permitted by temperature T, and no catalyst degradation or coking was observed.

Table III

HYDROGENATION OF UNFLUXED ASPHALTS—TOTAL
PRODUCT INSPECTIONS

Material	Feed, asphalt No. 1	Product, run No.			Feed, asphalt No. 2	Product, run No.		
		1	2	3		4	5	6
Gravity, ° API.....	0.1	2.8	4.3	5.2	0.6	2.9	4.5	5.6
Sulfur, weight percent.....	4.6	3.4	2.6	1.9	5.1	3.7	2.9	2.5
Naphtha insolubles, weight percent.....	17.9	15.0	12.7	12.3	12.3	8.6	7.2	6.4
Flash, P.M., ° F.....	240	235	280	-----	325	280	270	-----
Conradson carbon, weight percent.....	30.1	26.7	24.2	23.3	28.7	26.0	22.7	21.5
Viscosity, Furol, at—	-----	-----	-----	-----	-----	-----	-----	-----
210° F.....	6,530	1,681	629	-----	2,763	1,020	484	-----
275° F.....	610	195	130	-----	275	133	88	-----
325° F.....	616	102	75	32	223	80	43	30
375° F.....	93	-----	-----	-----	-----	-----	-----	-----
Ash, p.p.m.: Fe.....	347.1	89.3	57.5	42.5	38.4	15.8	7.5	4.1
Ni.....	27.1	38.1	30.2	26.8	46.4	43.7	39.2	36.5
Na.....	357	266	140	120	26.2	22.4	17.0	9.3
V.....	57.1	55.7	28.7	20.7	80.7	71.9	55.6	44.6
Softening point, ° F.....	1200	-----	-----	-----	1170	-----	-----	-----

¹ Approximately.

Substantial cracking of the asphalt took place as evidenced by the increasing gravity and decreasing viscosity of the successive products from a given run. It is also noted that substantial desulfurization occurred, the amount of desulfurization increasing from stage to stage in runs on a given feed stock. Desirable reduction in naphtha insolubles was also obtained. Ash contents of the products were considerably lower than those in either of the feed stocks.

The reduction in naphtha insolubles is considered to be quite striking for several reasons. Generally when operating with diluted asphalts, such as 50–50 mixtures of asphalt and heating oil, increase of naphtha insolubles is observed in the product, either by agglomeration of naphtha insolubles inherently present in the asphalt or those synthesized at the high temperatures employed.

In the case of the present runs when using an undiluted asphalt, dilution occurs as a result of cracking and/or hydrogenation of asphaltic material to lower boiling hydrocarbons, and there is no tendency to increase naphtha insolubles during the reaction. It appears that the large pore diameters and pore distribution of the catalyst used in these runs were potent factors responsible for this difference, apparently because the complex asphalt molecules were able to enter the active centers of the catalyst through the large pores, permitting the destruction of the complex asphalt molecules or colloids into smaller, less complex molecules.

Fuel oil blends were prepared from the products of runs 3 and 6 by fluxing with a catalytic heating oil (27.3° API, 200° F. flash point, 0.80 wt. percent sulfur) to a furol viscosity at 122° F. of 175. Inspections on the fuel oil blends are presented in Table IV below.

Table IV

	Asphalt No. 1	Total product from Run 3	Asphalt No. 2	Total product from Run 16
Vol. percent cat. htg. oil.....	50	33	44	31
Vol. percent asphalt.....	50	67	56	69
Furol viscosity at 122° F. SSF.....	175	175	175	175
Sulfur, weight percent.....	2.87	1.60	3.50	2.0

The blends containing treated asphalts met all of the common fuel oil specifications when using almost 70%

of the asphalt product in the blend. Blends using only 50% to 56% of the untreated asphalt could not meet sulfur specification.

Portions of the total product from runs 3 and 6 were processed by vacuum distillation to recover low boiling materials produced during the hydrogenation reaction. After distilling to a top vapor temperature of about 970° F. at 200 to 250 microns total pressure, the residua from each distillation were deasphalted at 170° F. using a 4:1 propane-butane solvent to oil ratio. The overall yields of liquid product from the conversion of the undiluted asphalt are shown in Table V below:

Table V

Yield of liquid products (on feed)	Feed stock			
	Asphalt No. 1, run 3		Asphalt No. 2, run 6	
	Weight percent	Vol. percent	Weight percent	Vol. percent
I.B.P., 650° F.....	3.9	4.7	2.6	3.1
650–960° F.1.....	19.4	20.5	15.5	16.6
Deasphalted Oil.....	6.8	7.4	7.4	7.9
Residual Asphalt.....	69.9	67.4	74.5	72.4
Total.....	100.0	100.0	100.0	100.0

¹ Cut point was 950° F. vapor temperature on run 3 product; 968° F. on run 6 product.

These data show that conversions to valuable products of from about 28 to 33 volume percent were obtained on the two asphalts. These are very significant conversions when taking into consideration the rather mild conditions used during the runs.

Inspections on the various fractions presented in Table V are shown in Table VI below:

Table VI

HYDROGENATION OF UNFLUXED ASPHALTS—INSPEC-
TIONS ON FRACTIONS DERIVED FROM VACUUM
DISTILLATION AND DEASPHALTING OF THIRD
STAGE PRODUCTS

Stock	Asphalt No. 1				
	Original asphalt feed	I.B.P.—650° F. VT	650° F.—950° F. VT	Deasphalted oil	Residual asphalt
Gravity, ° API.....	0.1	129.2	13.2	16.4	0.4
Sulfur, weight percent.....	4.60	10.110	0.78	0.96	2.69
Naphtha insolubles, weight percent.....	17.9	-----	-----	-----	19.9
Conradson carbon, weight percent.....	30.1	-----	0.85	6.1	32.8
Aromatics (by Si gel), weight percent.....	-----	175	72.2	-----	-----
	Asphalt No. 2				
	Original asphalt feed	I.B.P.—650° F. VT	650° F.—968° F. VT	Deasphalted oil	Residual asphalt
Gravity, ° API.....	0.6	129.0	14.9	16.1	1.5
Sulfur, weight percent.....	5.10	10.384	1.32	1.49	2.89
Naphtha insolubles, weight percent.....	12.3	-----	-----	-----	11.7
Conradson carbon, weight percent.....	28.7	-----	1.10	5.1	28.2
Aromatics (by Si gel), weight percent.....	-----	167	75.2	-----	-----

¹ Does not include about 20% of I.B.P.—650° F. fraction which consisted of nominal gasoline boiling range material.

It is noted that the deasphalted oil and asphalt from the products contained much less sulfur and had lower

Conradson carbon contents than the original asphalt. The various distillate fractions were indicated to contain relatively large portions of aromatic compounds as determined silica gel adsorption studies.

What is claimed is:

1. A process for hydrocracking an essentially asphaltic hydrocarbon feed stock containing less than about 15% of materials boiling below 1050° F., said asphaltic feed stock having the naphtha insolubles content in excess of about 5 weight percent, said process comprising the steps of contacting the said feed stock with a fixed bed of a porous solid hydrocracking catalyst in the presence of from about 500 to 6000 cubic feet of hydrogen per barrel of feed stock in a plurality of reaction zones operated in series at successively higher temperatures, at a pressure within the range of about 200 to 900 p.s.i.g., and at a space velocity within the range of about 0.25 to about 5 volumes of said feed stock per volume of catalyst per hour, said temperatures being within the range of about 650° to 825° F., the temperature in the first of said zones being sufficiently high to cause substantial hydrocracking but below the incipient coking temperature of the asphalt and being within the range of about 650° to 730° F. and the temperature in each succeeding zone being at least 5° F. higher than that in the immediately preceding zone, and the total effluent from a preceding zone being charged to an immediately succeeding zone.

2. A process as in claim 1 wherein the hydrogen charge rate is within the range of about 500 to 2000 cubic feet of hydrogen per barrel of feed stock and wherein the space velocity is within the range of 0.25 to 2 volumes of feed stock per volume of catalyst per hour.

3. A process for hydrocracking an essentially asphaltic feed stock containing less than about 15 percent of materials boiling below 1050° F. and having a naphtha insolubles content in excess of about 5 weight percent, said process comprising the step of contacting the asphaltic feed stock with a fixed bed of a porous solid hydrocracking catalyst in the presence of hydrogen in a plurality of reaction zones operated in series at successively higher temperatures at a pressure of less than about 1000 p.s.i.g., said temperatures being within the range of about 650° to 825° F., the temperature in the first of said zones being sufficiently high to cause substantial hydrocracking but below the incipient coking temperature of the asphalt and being within the range of about 650° to 730° F. and the temperature in each succeeding zone being at

least 5° F. higher than that in the immediately preceding zone, and the total effluent from a preceding zone being charged to an immediately succeeding zone.

4. A process for hydrocracking an essentially asphaltic feed stock containing less than about 15 percent of materials boiling below 1050° F. and having a naphtha insolubles content in excess of about 5 weight percent, said process comprising the step of contacting the asphaltic feed stock with a gamma alumina supported cobalt molybdate catalyst in the presence of hydrogen in a plurality of reaction zones operated in series at successively higher temperatures at a pressure of less than about 1000 p.s.i.g., and recovering from the last reaction zone at least a gas-oil fraction composed principally of hydrocarbon components boiling within the range of about 650° to 960° F., said temperatures being within the range of about 650° to 825° F., the temperature in the first of said zones being sufficiently high to cause substantial hydrocracking but below the incipient coking temperature of the asphalt and being within the range of about 650° to 730° F. and the temperature in each succeeding zone being at least 5° F. higher than that in the immediately preceding zone, and the total effluent from a preceding zone being charged to an immediately succeeding zone.

5. A process as in claim 4 wherein the reaction conditions in said zones include a pressure within the range of about 200 to 900 p.s.i.g., a hydrogen charge rate within the range of about 500 to 2000 cubic feet of hydrogen per barrel of feed stock and a space velocity of about 0.25 to 5 volumes of feed stock per volume of catalyst per hour.

6. A process as in claim 5 wherein the asphaltic feed stock is substantially completely free of components boiling below about 1050° F.

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