

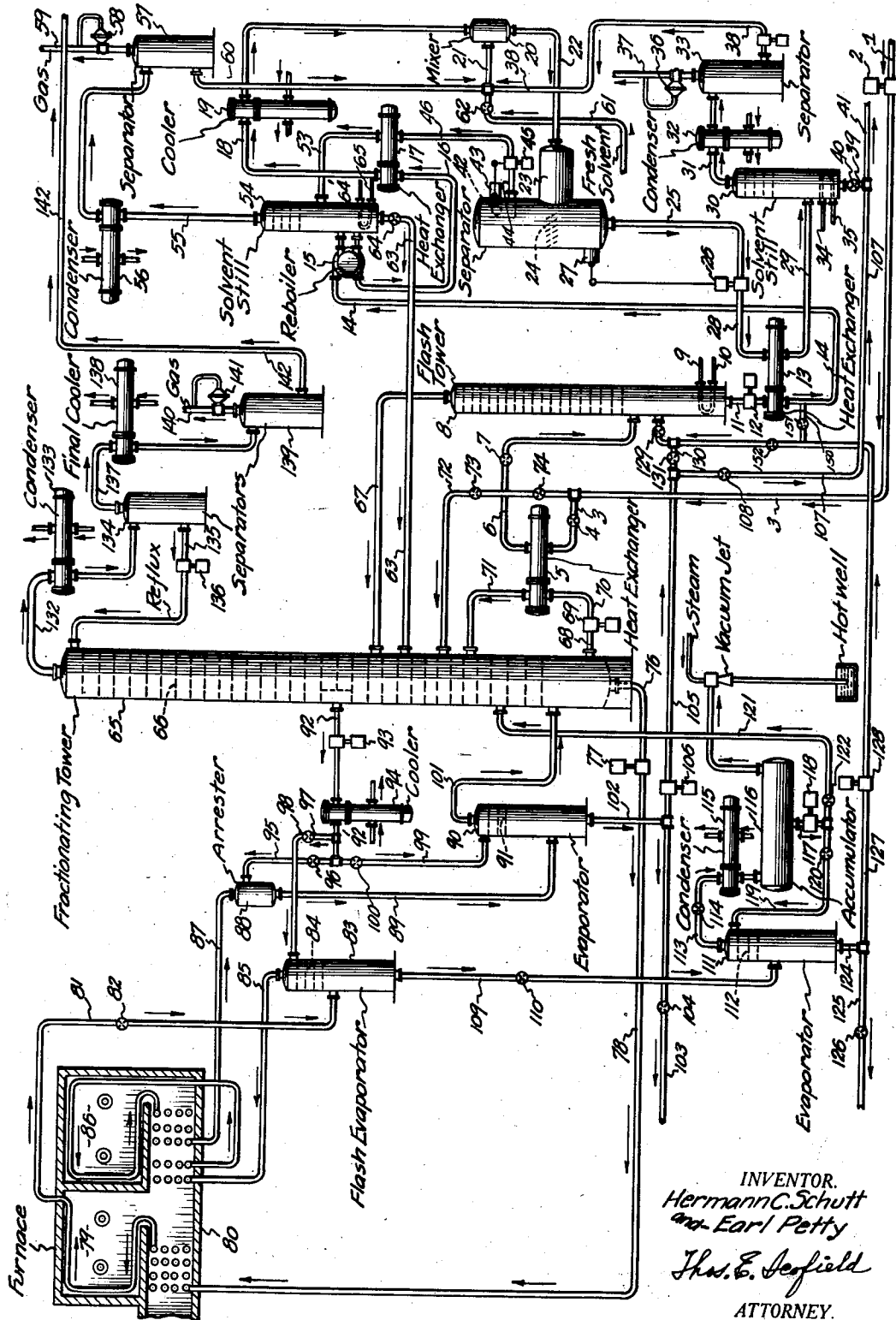
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PROCESS FOR CONVERTING HYDROCARBON OILS

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PROCESS FOR CONVERTING HYDRO-CARBON OILS

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This invention relates to the art of cracking hydrocarbon oils and more particularly to the recovery of a clean cracking stock from asphaltic or bitumen containing crude residuums and heavy tarry residuum of a cracking operation.

In the art of cracking, the amount of carbon in the stock being subjected to the cracking reaction determines the temperature limits and the economics of the process. Various methods have been used for segregating asphaltic and bituminous materials from the charging stock before it is subjected to the actual cracking reaction. For example, a clean primary distillate of low boiling range is sometimes used, or a residuum stock may be subjected to vacuum distillation to remove tar and carbonaceous materials. Still other systems combine the removal of carbonaceous materials with the cracking operation by zoning the process of heating preparatory to cracking into operations which may be generally classified as stripping, vacuum flashing, and viscosity breaking.

None of these methods for the pre-treatment of an asphaltic or bitumen containing charge is capable of effecting a sharp separation of the bituminous material and the oil. The bituminous material is always removed in either a residuum tar, or fuel oil, or as coke. This method is inconvenient, inefficient, and results in a loss of potential yield in all commercial operations.

The method of this invention provides a simple and effective means of overcoming these difficulties by an economical and efficient separation of the bituminous material without loss of valuable cracking stock. Heretofore the nearest approach to the method of this disclosure has been accomplished by a complete coking operation at high temperatures. The method to be described hereinafter gives all the yield benefits of the coking method and has the advantage that the excess carbon, bitumen, asphalt, or, more generally, the low hydrogen to carbon ratio constituents are removed at low temperatures by means of a well known anti-solvent for such materials.

It is known that if the excess carbon is removed from a cracking stock that the optimum balance of hydrogen to carbon may be obtained for conversion by the cracking reaction. By removing free carbon and the undesirable low hydrogen to carbon ratio constituents at a low temperature, the resultant product or raffinate will be composed of constituents having a sufficiently high hydrogen to carbon ratio to give not only improved yields of cracked products, but give improved ease of operation.

The lower the carbon number of a hydrocarbon

solvent, such as naphtha, pentane, butane, propane, ethane or methane, the more effective does that material become as an anti-solvent for carbonaceous or bituminous materials. When used in ratios, (liquid) of 4 to 8 times in volume, these anti-solvents are very effective in precipitating at normal temperatures such carbonaceous materials as tar, asphalt resins, etc. Conversely, these liquids are selective and protective in affinity for hydrogen. By selection of a solvent of the proper carbon number, it is possible to separate from the charging stock only those constituents whose presence is most undesirable. For example, certain intermediate resins and naphthenic materials are valuable for cracking and it is desirable not to carry the separation too far, since the raffinate may become even deficient in carbon when the overall make-up of the material to be cracked is considered. Accordingly, it is preferred that a carbon anti-solvent of about the carbon number of butane or a solvent in which butane is predominant be used. Such a solvent will produce a raffinate having a proper concentration of carbon and compounds of intermediate hydrogen to carbon ratio such as resinous asphaltines having some cracking value. If propane alone were used, these intermediate materials would be removed with the asphalt carbon compounds.

It is an object of this invention to provide in a process for cracking hydrocarbon oils a method of establishing in the cracking stock an optimum ratio of carbon and hydrogen for the cracking reaction while eliminating and segregating the excess free carbon and low hydrogen to carbon ratio constituents from the cracking stock in zones other than the high temperature heating and reaction zones.

It is another object of this invention to provide in a vapor phase process for cracking hydrocarbon oils a method of increasing the degree of vaporization in the evaporator for the same temperature and pressure conditions, to permit the use of higher operating temperatures in the viscosity breaking coil, to reduce the amount of primary fuel oil residue produced, to secure a greater yield of gas oil equivalent charge to the vapor phase cracking coil, and to reduce the amount of light gas formed.

It is a further object of this invention to provide in a process for cracking hydrocarbon oils a method for controlling the asphaltic and/or bituminous constituency of the charging stock to permit a greater cracking per pass and produce the optimum quantity of refractory fuel oil residue

which when blended with the natural asphalt of the oil will give an improved specification fuel oil as regards cold test.

It is a still further object of this invention to provide in a process for cracking hydrocarbon oils a method for producing a more nearly oil free and wax free bitumen that can be produced by conventional distillate separation processes and recovering the oil wax bearing fractions as cracking stock.

It is a further object of this invention to provide in a process for cracking hydrocarbon oils a method for producing from the bituminous constituents of the oil, a specification fuel oil of low cold test.

In the accompanying drawing which forms part of the instant specification and is to be read in conjunction therewith, the single figure is a schematic view of one form of apparatus capable of carrying out the process of this invention.

In general, the process of this invention contemplates the treatment of a cracking stock such as, for example, an asphaltic or bitumen containing reduced crude with a liquefied, normally gaseous hydrocarbon solvent and the separation from the cracking stock of insoluble free carbon, natural asphalt and bitumen to secure a gas oil equivalent charge for passage to the high temperature heating and reaction zones. These constituents forming the separated extract will be hereinafter referred to more generally as low hydrogen to carbon ratio constituents, it being understood, however, that this term is intended to include free carbon as well as asphaltic compounds having a low hydrogen to carbon ratio.

The clean charging stock or raffinate is then passed to a relatively low temperature heating or mild cracking zone where, if necessary, the raffinate may be subjected to a viscosity breaking operation and then flashed into a light vapor fraction and a relatively heavy liquid fraction forming a primary fuel oil. The light fraction is subjected to a relatively high temperature or more drastic cracking reaction after which there is separated from the cracked products a refractory fuel oil of low viscosity and high solvent power. The remaining vapor fraction of the cracked products is fractionated to recover a light distillate such as, for example, a motor fuel of gasoline boiling range.

The primary fuel is flashed at reduced pressure to recover the light gas oil remaining therein which is condensed and returned to the fractionator. The remainder of the primary fuel and the refractory fuel is passed to the solvent extraction zone wherein further separation of the fuels is made to recover a gas oil equivalent cycle stock while the asphaltic or bituminous constituents are rejected and removed with similar constituents of the fresh charge as a substantially oil and wax free bitumen.

If a residual operation is desired for the production of a low cold test fuel oil, the residue of the primary fuel is subjected to solvent extraction as has been described above while the refractory fuel is used for blending with the bitumen separated from the fresh charge and/or the primary fuel to form by virtue of its high solvent capacity a fuel oil of extremely low cold test.

Referring now more particularly to the drawing, the charging stock consisting of, for example, an asphaltic reduced crude, is fed through a line 1 to a pump 2 which discharges the oil

under pressure through a line 3 controlled by a valve 4 to a heat exchanger 5. The charging stock is heated in this exchanger and is discharged therefrom through a line 6 controlled by a valve 7 to a flash or distillation tower 8 wherein a separation of the oil into vapors and unvaporized oil takes place. The flash tower may be provided with a suitable number of baffle plates or fractionating trays and the degree of vaporization may be controlled by means of a heating coil in the tower to which steam or other heating medium may be admitted through a line 9 and be removed through a line 10.

The unvaporized oil, free of those light ends suitable as cracking material without solvent treating, is withdrawn from the flash tower 8 through a line 11 and is pumped by pump 12 at a pressure of from 100 to 150 lbs. per square inch through a heat exchanger 13, wherein the oil is slightly cooled and then passes through a line 14 to a conventional reboiler 15 of a solvent stripping tower 54 where some of the heat of the untreated oil is given up in stripping solvent from treated oil. The further cooled oil leaves the reboiler through a line 16, passes through a heat exchanger 17 wherein it is further cooled by indirect heat exchange with oil-solvent solution passing to the stripping tower, and on leaving the heat exchanger 17 passes through a line 18 and cooler 19 to a mixing chamber 20. A final cooling of the oil to a favorable solvent treating temperature, for example 70°-120° F., is effected in the cooler 19. The mixing chamber 20 may be equipped with suitable baffles, or mechanical agitating devices (not shown) for securing proper admixture of oil and solvent, solvent under pressure being introduced to the mixing device through a line 21. A liquefied, normally gaseous hydrocarbon such as butane, or butane admixed with varying proportions of lighter normally gaseous hydrocarbons, is used as the solvent. The specific references to a particular hydrocarbon solvent are illustrative only, and it will be understood that the character of the charging stock as regards its content of asphaltic or bituminous concentrates, the percent of resinous naphthenes whose removal is desired, and/or the desired freedom of asphalt from oil will govern the character and amount of the solvent to be used. However, sufficient of a selective solvent should be admixed with the oil to precipitate the amount and kind of constituents not suitable for cracking it is desired to remove and the ratio of solvent to oil may be, for example, four to ten parts of solvent by volume to one part of oil.

The oil-solvent mixture containing insoluble constituents leaves the mixing device 20 and passes under pressure through a line 22 to a bitumen separator or settling tank 23.

The separator 23 is of sufficient size to permit the establishment of the time element necessary to secure separation of the insoluble constituents from the oil solvent solution. The bitumen collects in the lower portion of the separator while the supernatant oil solvent solution free of bitumen forms a layer above the bitumen. A baffle 24 or other suitable device for preventing intermixture of the bitumen and oil is suitably positioned within the separator.

The bitumen collecting in the bottom of the separator 24 discharges through a line 25 to the suction side of a pump 26. The pump may be manually controlled or automatic means diagrammatically indicated at 27 may be provided for controlling the pump and the withdrawal

rate in accordance with the viscosity of the bitumen being removed. The bitumen is forced by means of the pump 26 through a line 28, through the heat exchanger 13, picking up a certain amount of heat from the hot untreated oil discharged from the flash tower 8 and then is forced through a line 29 to a solvent stripping tower 30 wherein by the application of heat, solvent is distilled from the bitumen, the solvent vapors under considerable pressure passing overhead through a line 31, being condensed in a condenser 32 and the liquid discharging into a pressure accumulator 33. The stripping tower 30 is provided with a heating coil, steam or other suitable heating medium being introduced thereto through a line 34 and removed through a line 35.

The pressure accumulator 33 is maintained at the desired condensing pressure by means of a back pressure control valve 36 in a vent line 37. The solvent liquid accumulating in the accumulator 33 discharges therefrom under pressure through a line 38 being returned thereby to the line 21 for reuse in the system.

The bitumen in the tower 30 free of wax oil and solvent discharges from the tower through a line 39 controlled by a valve 40 and passes therefrom through a line 41 to storage tanks (not shown).

The bitumen free oil solvent solution in the separator 23 overflows into an internal chamber 42 in which a constant liquid level is maintained by a liquid level control device generally indicated at 43. The oil solvent solution discharges from the chamber 42 through a line 44 to the suction side of a pump 45. Although the pump 45 may be manually controlled, it is preferably controlled by the liquid level control device 43 in a manner well known in the art. The oil solvent solution is discharged under considerable pressure by the pump 45 through a line 46 and passes through the heat exchanger 17 from which it passes through a line 53 to a solvent stripping tower 54.

Although we have shown a bitumen separator 23 functioning to remove the bitumen from the oil solvent solution by gravity, it is within the contemplation of our invention to substitute therefor a continuous centrifugal separator operating under pressure.

Solvent is stripped from the solution in the tower 54 by means of the reboiler 15 and a heating coil into which a heating medium is fed from a line 64' and removed through a line 65. The solvent vapors pass overhead through a line 55, being condensed in a cooler 56, the condensate passing to a pressure accumulator 57 in which a back pressure is maintained by means of a pressure regulator 58 in a gas vent line 59. The solvent liquid discharges under pressure from the accumulator 57 and passes through a line 60 to the line 21 for reuse in the process. Further solvent may be added to the line 21 through a line 61 connected to a source of solvent supply by manipulation of the control valve 62.

The treated oil is discharged under the pressure in the solvent stripping tower 54 through a line 63 controlled by a valve 64 and fed to a fractionating tower 65 equipped with the usual fractionating trays 66. At the same time oil vapors separated from the charging stock in the flash tower 8 are fed through the line 67 to the fractionator 65.

The hot liquid bottoms in the fractionating tower are withdrawn through a line 68 by means of a pump 69 and pumped through a line 70 through the heat exchanger 5 to impart heat

to the charging stock and returned to the fractionating tower through a line 71. If desired, the initial solvent treating of the charging stock may be dispensed with in part, by manipulation of the valves 7 and 74 in the lines 6 and 3 respectively, permitting part of the charging stock to flow from the line 3 through a line 72 controlled by a valve 73 to the fractionating tower 65.

The bottoms in the fractionating tower consisting of reflux condensate, cycle stock, and charge oil are withdrawn through a line 76 and pumped by means of the pump 77 through a line 78 to a low temperature primary heating, viscosity breaking, or mild cracking section 79 of a cracking furnace 80 from which the heated oil discharges through the line 81 to a primary evaporator 83 at a lower pressure, provided with a suitable number of fractionating trays 84. The pressure on the oil discharging through the line 81 is reduced by means of a reducing valve 82 so that a controlled amount of flash vaporization will take place in the evaporator 83 due to the sensible heat of the hot oil.

The vapors evolved in the evaporator 83 pass off overhead through a line 85, through a high temperature vapor phase cracking section 86 of the cracking furnace 80, discharging therefrom through a line 87 to an arrester 88. The vapors are quenched in the arrester 88 below active vapor phase cracking temperature by means of a cool hydrocarbon oil, the quenched products passing through a line 89 to a flash tower 90 equipped with a suitable number of fractionating trays 91.

A clean side stream distillate is withdrawn from a suitable tray of the fractionating tower 65 through a line 92, a portion being pumped by means of a pump 93 through a cooler 94, the cooled distillate being diverted in part through a line 95 controlled by a valve 96 to the arrester 88 for use as the quenching medium. The remainder of the cooled distillate passing through the line 92 is fed through a line 99 controlled by a valve 100 to the flash tower 90 where it serves as reflux for endpoint control and to knock back heavy ends unsuitable for recycling. Another portion of the side stream is diverted through a line 97 controlled by a valve 98 to the primary evaporator 83 wherein the cooled side stream acts as reflux for fractionation control in the same manner.

The light vapors passing overhead from the flash tower 90 are removed through a line 101, and introduced at a suitable point into the fractionating tower 65 wherein a separation of cycle stock from the vapors is carried out.

The unvaporized oil in the flash tower 90 generally unsuitable for recycling because of its low hydrogen to carbon ratio consists of a refractory fuel oil which because of its comparatively low viscosity has a high blending power and is withdrawn therefrom through a line 102 and may, if desired, be diverted without further treatment through the line 103 controlled by a valve 104 to storage tanks (not shown). However, if solvent treatment of this refractory fuel oil is desired for the purpose of recovering additional cracking stock therefrom, it may be diverted from the line 102 through a line 105 and pumped by means of a pump 106 through a line 130 controlled by a valve 131 and returned through a line 127 controlled by a valve 129 to the flash tower 8. This fuel oil being at a relatively high temperature will aid in vaporizing the light ends

of the charging stock being fed to the flash tower 8 through the line 6 for solvent treating or, if desired, the fuel oil may be solvent treated separately from the charging stock for removal of the asphaltic or bituminous material contained therein, the treated oil after being stripped of solvent being returned to the fractionating tower as cycle stock.

Preferably, however, the high blending power of the untreated refractory fuel oil may be advantageously utilized by diverting the oil from the line 105 through a line 107 joining the line 41 by opening a valve 108 in the line 107 and closing the valve 131 in the line 130, the oil thus being blended with oil and wax free bitumens recovered by solvent treating of the charge and/or primary fuel oil and issuing from the solvent stripping tower 30 through the line 39 to form a blended specification fuel oil of low cold test.

The primary fuel oil in the evaporator 83 discharges under pressure through a line 109 controlled by a valve 110 to a secondary evaporator 111 provided with a suitable number of fractionating trays 112. This secondary evaporator is preferably maintained at a somewhat lower pressure than exists in the primary evaporator 83 and there will be, therefore, a flash vaporization occurring, oil vapors passing overhead through a line 113 controlled by a valve 114, through a condenser 115, condensate formed therein being collected in a reflux accumulator 116. Condensate is withdrawn from this accumulator through a line 117 and is pumped in part by means of a pump 118, through a line 119 controlled by a valve 120 to the secondary evaporator 111 to serve as reflux for endpoint control on the fractionating trays 112. The remainder of the condensate is pumped through a line 121 controlled by a valve 122 to the fractionating tower 65 for recycling in the cracking furnace.

The unvaporized fuel oil in the secondary evaporator 111 still contains some heavy cycle stock and being at a comparatively high temperature, is withdrawn through a line 124 and, if desired, may be passed without further treatment through a line 125 controlled by a valve 126 to storage tanks (not shown).

Preferably, however, since this fuel oil still contains considerable cracking stock whose recovery is desirable in order to maintain a high yield the fuel oil is pumped through a line 127 by means of a pump 128 to the flash tower 8 for recycling to the solvent treating plant, its heat content being imparted to the fresh feed and aiding in the distillation of the initial charging stock if this material is also being subjected to solvent treatment. If desired, this fuel oil in pipe 127 may be fed through a pipe 150 into pipe 14 by opening valve 151 and closing valve 152 in pipe 127 thus bypassing the flash tower 8 in which charging stock only will then be distilled. The bitumen separated from this fuel oil will be substantially oil and wax free and is recovered with the bitumen separated from the charging stock although if desired the fuel oil may be separately solvent treated for bitumen separation. The bitumen is then blended with the refractory fuel oil to form a low cold test fuel oil as has been previously pointed out.

The vapors of desired endpoint remaining uncondensed in the fractionating tower 65 pass overhead through a line 132, a portion being condensed in a cooler 133, the condensate and vapors

being collected in a reflux accumulator 134. Reflux is returned from this accumulator through a line 135 by means of the pump 136 to the fractionating tower 65. The vapors passing overhead from the accumulator 134 are removed through a line 137, are condensed in a final cooler 138, and accumulated in a separator 139. The uncondensable gases are removed through a line 140, a back pressure being maintained by a regulating valve 141, the distillate being removed as a liquid from the separator 139 through the line 142 and passed to a stabilizer feed tank (not shown).

It will be observed that we have accomplished the objects of our invention and have provided a process by which the character of the charging stock may be controlled to provide an optimum balance of hydrogen to carbon in the charging stock and by which the asphaltic and bituminous concentrates of the oil may be removed at relatively low temperatures in zones other than the high temperature cracking or heating zones. We have also provided a process by which a more nearly oil-free and wax-free bitumen is produced than has heretofore been possible by conventional distillation methods and by which a fuel oil of low cold test is secured by blending the low viscosity refractory fuel oil with the wax-free bitumen separated by solvent extraction. We are also enabled by our process because of the lesser amount of low hydrogen to carbon ratio hydrocarbons to secure an increased yield of lower boiling hydrocarbon distillate of high octane from the original charging stock by using higher temperatures without danger of coke deposition in the conversion coils.

It will be understood that certain features and sub-combinations are of utility and may be employed without reference to other features and sub-combinations. This is contemplated by and is within the scope of our claims. It is further obvious that various changes may be made in details within the scope of our claims without departing from the spirit of our invention. It is, therefore, to be understood that our invention is not to be limited to the specific details shown and described.

Having thus described the invention, what we claim is:

1. A process for cracking hydrocarbon oil comprising treating charge oil with a diluent in which bituminous constituents of the oil are substantially insoluble, removing the undissolved constituents from the oil, fractionating the treated oil in a fractionating zone, subjecting reflux condensate withdrawn from the fractionating zone to mild pyrolytic conversion in a relatively low temperature conversion zone, separating the heated oil into a primary residue and a relatively light fraction, subjecting the light fraction to more drastic pyrolytic conversion in a relatively high temperature conversion zone, separating the products of the high temperature conversion operation into a light fraction and a relatively heavier secondary residue, returning the last mentioned light fraction to the fractionating zone, withdrawing the secondary residue from the process and combining the primary residue with the oil passing to the solvent treating zone.

2. The process of claim 1 wherein the diluent comprises normally gaseous hydrocarbons.

3. The process of claim 1 including the step of blending the secondary residue with the insoluble

constituents removed from the oil to form a low cold test fuel oil.

4. A process for cracking hydrocarbon oil comprising distilling fresh oil in a distillation zone and there separating the oil into vapors and unvaporized oil, separately removing the vapors and unvaporized oil from the distillation zone, treating the unvaporized oil with a solvent in which the oil constituents relatively rich in hydrogen are soluble and constituents relatively poor in hydrogen are substantially insoluble, separating the undissolved compounds from the oil-solvent solution, distilling the solvent from the oil, fractionating the solvent free oil in a fractionating zone, passing a stream of reflux condensate from the fractionating zone to a heating zone and subjecting the oil to a mild cracking reaction at a relatively low temperature, separating the heated oil into light products and a relatively heavier primary residue, heating the light products in a separate heating zone and subjecting them to a more drastic cracking reaction at a relatively higher temperature, separating the products from

the high temperature cracking reaction into a vapor fraction and a secondary residue, fractionating the vapor fraction in the fractionating zone, and distilling the primary residue in the distillation zone.

5. The process of claim 4 including the step of combining the primary residue with the unvaporized oil removed from the distillation zone rather than with the fresh oil in the distillation zone.

6. The process of claim 4 including the step of heating the fresh oil by heat exchange relationship with reflux condensate from the fractionating zone before introducing the fresh oil to the distillation zone.

7. The process of claim 4 including the step of distilling the solvent from the undissolved constituents separated from the oil solvent solution and blending these constituents with the secondary residue to form a low cold test fuel oil.

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