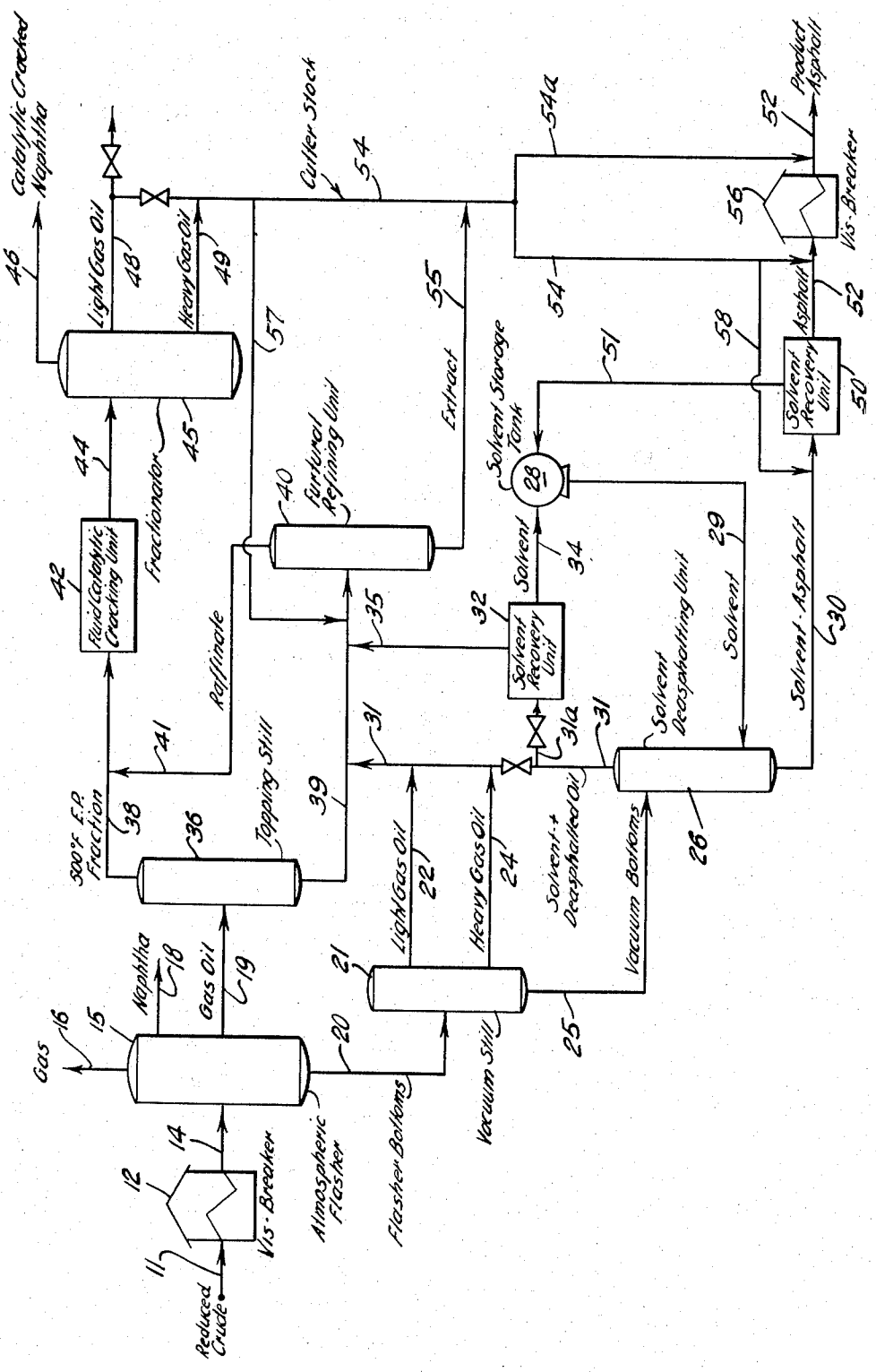
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TREATMENT OF RESIDUAL ASPHALTIC OILS WITH LIGHT HYDROCARBONS

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TREATMENT OF RESIDUAL ASPHALTIC OILS WITH LIGHT HYDROCARBONS

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This invention is related to the treatment of residual asphaltic oils with light hydrocarbons for the separation of asphaltic constituents therefrom. More particularly, this invention is concerned with the treatment of asphaltic residual hydrocarbon oils for the recovery of the asphaltic constituents therefrom and for the production of a deasphalted oil suitable for use as a catalytic cracking feed stock. In accordance with one embodiment this invention relates to a process for deasphalting residual hydrocarbon oils for the production of an asphalt fraction and a deasphalted oil fraction which is subsequently treated in accordance with the practice of this invention for the production of a catalytic cracking feed stock characterized by a relatively low metals content.

It is an object of this invention to provide an improved process for the treatment of residual asphaltic hydrocarbon oils.

It is another object of this invention to provide a process for the treatment of residual asphaltic hydrocarbon oils with liquid low molecular weight hydrocarbons, such as liquefied normally gaseous hydrocarbons, for the production of an asphalt fraction and a deasphalted oil fraction particularly suitable as catalytic cracking feed stock.

It is still another object of this invention to provide a process for the treatment of residual asphaltic hydrocarbon oils wherein there is recovered a deasphalted oil fraction having a relatively reduced metals content and which is particularly suitable for use as a catalytic cracking charge stock.

How these and other objects of this invention are accomplished will become apparent with reference to the accompanying disclosure and drawing wherein there is schematically illustrated an embodiment of the practice of this invention.

Referring now in detail to the drawing a reduced crude, such as a mixture of reduced California crudes having an initial boiling point greater than about 650° F., usually having a boiling point higher than about 800° F., amounting to about 35–75% by volume of the original crude, is supplied via line **11** to vis-breaking zone **12** where it is subjected to temperature, pressure and throughput conditions so as to mildly lower the viscosity of the reduced crude. Vis-breaking conditions in the temperature range 800–1000° F., and pressures in the range 50–800 p. s. i. g., are usually sufficient to effect mild vis-breaking of the reduced crude.

Vis-breaking of the reduced crude serves to reform or otherwise alter the high molecular weight or high boiling constituents of the reduced crude into relatively low molecular weight or low boiling constituents. The vis-breaking operation tends to produce lower boiling, more aromatic constituents which are generally more refractory in a catalytic cracking operation than lower boiling, more paraffinic hydrocarbons which are also produced. The vis-breaking operation complements and otherwise cooperates with a subsequent combination of deasphalting and solvent refining operations in accordance with this invention and described hereinafter. The

vis-breaking operation increases the yield of naphtha recoverable from the reduced crude in that the relatively more aromatic hydrocarbons produced during the vis-breaking operations are separated in subsequent combination fractionation and deasphalting solvent-refining steps with the resulting production of a more paraffinic catalytic cracking charge stock more suitable for the production of a catalytic cracked naphtha.

The mildly vis-broken reduced crude from vis-breaking zone **12** is introduced via line **14** into fractionator or atmospheric flasher **15** where there is recovered overhead via line **16** a gas fraction comprising normally gaseous hydrocarbons, such as propane and the butanes, a naphtha fraction via line **18**, such as a 430° F. end point naphtha, and a gas oil fraction via line **19**. There is also recovered from flasher **15** a bottoms fraction via line **20**. The flasher bottoms fraction is then introduced into a vacuum fractionation or distillation zone **21** where it undergoes further fractionation for the production of a light gas oil fraction recovered via line **22** and a heavy gas oil fraction recovered via line **24**. A vacuum bottoms fraction is recovered from vacuum fractionator **21** via line **25**.

The vacuum bottoms fraction recovered from vacuum fractionator **21** via line **25** usually having a gravity °A. P. I. in the range 3–12 and a Conradson Carbon residue in the range 15–40%, more or less, is introduced into the upper part of solvent deasphalting tower or zone **26**. The solvent deasphalting operation may be a batch operation, a multiple vessel operation or a substantially continuous liquid-liquid countercurrent treating operation, as indicated in the drawing, wherein the vacuum bottoms to be deasphalted is introduced via line **25** into the top of deasphalting tower **26** and flowed therein in liquid-liquid countercurrent contact with a suitable deasphalting solvent, such as a liquefied normally gaseous hydrocarbon, e. g., propane, n-butane, isobutane. The deasphalting solvent is introduced via line **29** into the bottom portion of deasphalting tower **26** from deasphalting solvent storage tank **28**.

A suitable deasphalting solvent in accordance with the practice of this invention is a liquefied normally gaseous hydrocarbon such as ethane, ethylene, propane, propylene, normal butane, isobutane, n-butylene, isobutylene, pentane, isopentane and mixtures thereof, either alone or in the presence of a minor amount of additive materials to improve the deasphalting operation or otherwise increase the yield and quality of the deasphalted oil and/or the recovered asphalt. The deasphalting operation is carried out at any suitable deasphalting temperature and pressure, the temperature and pressure being adjusted so as to maintain the deasphalting solvent in the liquid phase during the deasphalting operation. A deasphalting temperature in the range 150–325° F., usually not more than 75 degrees Fahrenheit lower than the critical temperature of the deasphalting solvent, and a pressure in the range 300–800 p. s. i. g. are employed depending upon the composition of the deasphalting solvent, and to a minor extent depending upon the composition of the vacuum bottoms undergoing deasphalting. Generally, a deasphalting solvent to vacuum bottoms volume ratio in the range 10–2 is employed within deasphalter **26**. Deasphalter **26** may be operated isothermally or under a temperature gradient, top tower temperature greater than bottom tower temperature by not more than about 40 degrees Fahrenheit. Also deasphalter **26** may be operated so that the vacuum bottoms is introduced thereinto at a number of points along the height of deasphalter **26** and/or the deasphalting solvent is introduced at a number of points.

Following the deasphalting operation there is recovered from deasphalter **26** a solvent deasphalted oil mix via

line 31 and a solvent asphalt mix via line 30. The deasphalted oil in the mix may have a gravity ° A. P. I. in the range 10–25 and a Conradson Carbon residue in the range 1–10% and a viscosity in the range 200–600 SUS @ 210° F., more or less. The solvent deasphalted oil mix is introduced via line 31*a* into deasphalted oil solvent recovery zone 32 wherein at least a portion or substantially all of the deasphalting solvent is removed from the deasphalted oil and returned to deasphalting solvent storage tank 28 via line 34. The resulting deasphalted oil is recovered via line 35. If desired, the solvent deasphalted oil mix may be treated, as indicated, substantially as recovered from deasphalter 26 via line 31 since the presence of a light hydrocarbon during the subsequent solvent refining operation appears to enhance the removal of metals from the deasphalted oil, thereby producing a better catalytic cracking charge stock. The light hydrocarbon present during the solvent refining operation may be the deasphalting solvent itself or an extraneous, different light hydrocarbon, e. g., a pentane when the deasphalting solvent is a butane such as n-butane or isobutane.

Referring now to the gas oil fraction recovered from atmospheric flasher 15 via line 19, this gas oil fraction is introduced into topping still 36 where there is produced overhead via line 38 a fraction having an end point of about 500° F., this overhead fraction being particularly suitable as a catalytic cracking charge stock. The bottoms fraction recovered from topping still 36 via line 39 is combined with the gas oil fractions recovered from vacuum fractionator 21 via lines 22 and 24 and with the solvent deasphalted oil mix recovered directly from deasphalter 26 via line 31 or with the deasphalted oil having a reduced amount of deasphalting solvent recovered from solvent recovery unit 32 via line 35 (metals content, such as vanadium, nickel, copper and iron, of the resulting combined stream in the range 5–15 p. p. m.) and introduced into solvent refining unit 40 wherein it flows in liquid-liquid countercurrent contact with a liquid selective solvent, such as furfural, which selectively dissolves the more aromatic hydrocarbons therefrom. The resulting raffinate (having a reduced metals content, e. g., metals content in the range 0.2–5 p. p. m.), after having been freed of its selective solvent content, is recovered from solvent refining unit 40 and is combined via line 41 with the 500° F. end point overhead fraction recovered from topping still 36 via line 38 and introduced as feed stock to fluid catalytic cracking unit 42 where it is contacted with fluidized catalytic cracking catalyst. These cracking catalysts are usually oxides of metals of groups II, III, IV and V of the periodic table.

A suitable cracking catalyst comprises a silica-alumina catalyst containing about 5–30% by weight alumia. The average particle size of the cracking catalyst particles is usually below about 200 microns, a size sufficient to produce a dense fluidized bed of cracking catalyst. The resulting catalytic cracked effluent from fluid catalytic cracking unit 42 is introduced via line 44 into fractionator 45 wherein it is fractionated into a catalytic cracked naphtha recovered via line 46, a catalytic cracked light gas oil recovered via line 48 and a relatively heavy cycle gas oil recovered via line 49.

The solvent asphalt mix is recovered from deasphalter 26 via line 30 and introduced into asphalt solvent recovery zone 50 wherein deasphalting solvent is recovered via line 51 for return to deasphalting solvent storage tank 28. The resulting substantially solvent-free asphalt recovered from asphalt solvent recovery zone 50 via line 52, which asphalt may have a ring and ball softening point in the range 180–325° F., is combined with at least a portion of the gas oil fractions recovered from catalytic cracking fractionator 45 via lines 48, 49 and 54. To this combined stream is added the selective solvent-free extract recovered from solvent refining zone 40 via line 55, the resulting stream of combined catalytic cracked gas oils and selective solvent extract being added via line 54 as cutter stock to the substantially solvent-free asphalt. In accordance with one feature of this invention at least a portion of the light gas oil recovered via line 48 and/or the heavy gas oil recovered via line 49 are passed via lines 54 and 57 to solvent refining unit 40 for the recovery of the more paraffinic constituents therefrom as raffinate via line 41 as aditional catalytic cracking charge stock and for the recovery of the more aromatic constituents therefrom as extract via line 55 as cutter stock. By operating in accordance with this feature of the invention the yield of recoverable catalytic cracked naphtha is further increased.

Desirably, especially when a particularly heavy crude such as San Ardo California crude is the source of the reduced crude introduced into the above-described operations via line 11, the asphalt in line 52, prior to the addition of cutter stock thereto via line 54*a*, is subjected to vis-breaking, as indicated by vis-breaking zone 56 in the drawing. Desirably, also, a portion of the combined stream employed as cutter stock is admixed via line 58 with the solvent asphalt mix recovered from deasphalter 26 via line 31 prior to introducing the same into asphalt solvent recovery zone 50 for the recovery of the deasphalting solvent therefrom. This addition of cutter stock to the solvent asphalt mix prior to introduction into the asphalt solvent recovery system is desirable in order to alleviate coke deposition and reduce cracking which might occur within the furnace heating tubes and upon the heated surfaces employed within the asphalt solvent recovery system.

The following is illustrative of the practice of this invention. A mixture comprising California crudes was atmospherically distilled to about 50–55% volume reduced crude based on the original crude mixture and charged through a heater operated under mild viscosity-breaking conditions at an outlet temperature of 850° F. The resulting mildly viscosity-broken reduced crude was introduced into an atmospheric flasher from which was recovered overhead approximately a 46% volume yield of gas, naphtha and atmospheric viscosity-broken gas oil, basis reduced crude, in the following amounts: gas 1% volume; 430° F. end point naphtha 3.5% volume; gas oil 41.5% volume, the atmospheric flasher being operated at a maximum temperature of about 790–800° F. The remaining atmospheric flasher bottoms having a gravity of about 12 ° A. P. I. and a Conradson Carbon residue of about 15 was introduced into a vacuum still operated at about 25 mm. Hg and at a temperature of 665° F. There was recovered overhead from the vacuum still gas oil fractions amounting to about 42% by volume of the vacuum still charge. There was recovered from the vacuum still a heavy bottoms fraction amounting to about 16% by volume basis original crude mixture or about 33.8% by volume basis reduced crude. The vacuum still bottoms has a gravity of about 3.6 ° A. P. I., a penctration (100 gm./5 sec./77° F. cm.$\times 10^{-2}$) about 27–29 and a Conradson Carbon residue in the range 26–33.

A vacuum still bottoms fraction was solvent deasphalted, employing liquid isobutane as the deasphalting solvent and a solvent:oil volume ratio of 5:1 at a temperature in the range 235–245° F., more particularly at about 243° F., and a pressure in the range 350–385 p. s. i. g. There was recovered from the above deasphalting operation a deasphalted oil at a yield of about 42% by volume basis deasphalting charge stock. The resulting deasphalted oil had a gravity in the range 15.3–16.8° A. P. I., a viscosity SUS 210° F. in the range 238–281, a Conradson Carbon residue in the range 4.1–5.0 and a K factor of about 11.70.

A high boiling petroleum fraction comparable to the deasphalted oil recovered from the aforesaid deasphalting operation was subjected to liquid-liquid furfural solvent refining at various dosages of furfural and in the

presence of an added liquid light paraffinic hydrocarbon, viz, n-pentane, suitable for use as a deasphalting solvent, the paraffinic hydrocarbon being added in an amount in the range 0.5–10.0 volumes per volume of petroleum fraction being thus treated. Prior to furfural solvent refining the high boiling petroleum fraction had a metals content (Ni+V) of about 2.3 p. p. m. Portions of the same oil were also subjected to furfural refining in the absence of added liquid light hydrocarbon. The metals content of the resulting furfural refining oil recovered after each of these tests were determined. The metals content as determined by these tests is set forth in the accompanying Table 1.

Table 1

Solvent	Solvent Dosage, Vol. Percent	Pentane Dilution	
		None	4:1
None		[1] 2.3	[1] 2.2
Furfural	100	1.7	0.25
Furfural	200	1.1	0.15

[1] Metals content in p. p. m. on recovered stripped oils.

The above table indicates that a heavy oil fraction, such as a heavy deasphalted oil containing a substantial amount of metals, such as a metals content (vanadium + nickel) in the range 10–25 p. p. m., more or less, can be treated in accordance with the practice of this invention by solvent refining, such as by furfural solvent refining, in the presence of a liquid light hydrocarbon, such as a liquefied normally gaseous hydrocarbon suitable for deasphalting, to produce a raffinate which is particularly suitable for use as charge stock to a fluid catalytic cracking unit, not only by virtue of its relatively paraffinic character but also by virtue of the fact that the raffinate contains a relatively low metals conent, particularly with respect to those metals which are undesirable in a feed stock to a fluid catalytic cracking operation because of their propensity to deactivate or reduce the activity of the cracking catalyst.

There was recovered from the aforesaid deasphalting operation an asphalt having a ring and ball softening point in the range 200–300° F.

As will be apparent to those skilled in the art in the light of the foregoing, many substitutions, changes and alternations are possible in the practice of this invention without departing from the spirit or scope thereof.

I claim:

1. A process for treating a residual oil containing asphaltic constituents which comprises heating said oil to an elevated temperature under vis-breaking conditions, fractionating the resulting vis-broken oil to yield a first gas oil fraction and a first bottoms fraction, fractionating said first bottoms fraction to produce a second gas oil fraction and a second bottoms fraction, fractionating said first gas oil fraction to separate therefrom constituents having a boiling point not greater than about 500° F. and to yield a third bottoms fraction, subjecting said second bottoms fraction to liquid-liquid contact with a liquid deasphalting solvent under deasphalting conditions to separate asphaltic constituents from said second bottoms fraction and to yield a deasphalted oil fraction, combining said third bottoms fraction, said second gas oil fraction and said deasphalted oil fraction, subjecting the resulting combined fractions to liquid-liquid solvent refining in contact with a liquid solvent which is a selective solvent for relatively more aromatic hydrocarbons, recovering from the aforesaid solvent refining operation a raffinate having a reduced amount of relatively more aromatic hydrocarbons relative to said resulting combined fractions and an extract having an increased amount of relatively more aromatic hydrocarbons relative to said resulting combined fractions, combining said raffinate with said constituents having a boiling point not greater than about 500° F., and subjecting the resulting combined stream to catalytic cracking.

2. A process in accordance with claim 1 wherein said elevated temperature is in the range 750–1000° F. and wherein said deasphalting solvent comprises a hydrocarbon selected from the group consisting of propane, normal butane, isobutane, normal pentane and isopentane.

3. A process in accordance with claim 1 wherein said solvent refining operation is carried out in the presence of said deasphalting solvent.

4. A process in accordance with claim 1 wherein said deasphalting solvent comprises isobutane.

5. A process in accordance with claim 1 wherein said deasphalting solvent comprises isobutane and wherein said selective solvent is furfural.

6. A process for treating an asphaltic residual oil which comprises heating said oil to an elevated temperature under vis-breaking conditions, fractionating the resulting vis-broken oil to yield a first gas oil fraction and a first bottoms fraction, fractionating said first bottoms fraction to produce a second gas oil fraction and a second bottoms fraction, fractionating said first gas oil fraction to separate therefrom hydrocarbons having a boiling point not greater than about 500° F. and to yield a third bottoms fraction, subjecting said second bottoms fraction to liquid-liquid contact with a liquefied normally gaseous hydrocarbon under deasphalting conditions to separate asphaltic constituents from said second bottoms fraction and to yield a deasphalted oil fraction, combining said third bottoms fraction, said second gas oil fraction and said deasphalted oil fraction, subjecting the resulting combined fractions to liquid-liquid solvent refining in contact with a liquid solvent immiscible with said resulting combined fractions and which is a selective solvent for relatively more aromatic hydrocarbons, recovering from the aforesaid solvent refining operation a raffinate having a reduced amount of more aromatic hydrocarbons and a lowered metals content relative to said resulting combined fractions and an extract having an increased amount of more aromatic hydrocarbons relative to said resulting combined fractions, combining said raffinate with said constituents having a boiling point not greater than about 500° F., subjecting the resulting combined stream to catalytic cracking, separating from the resulting catalytic cracked effluent a cracked gas oil fraction and admixing said extract and said cracked gas oil fraction with the asphaltic constituents separated from the aforesaid deasphalting operation.

7. A process in accordance with claim 6 wherein said elevated temperature is about 850° F., wherein said liquefied normally gaseous hydrocarbon is a C_4 hydrocarbon, wherein said selective solvent is furfural and wherein the deasphalting conditions are such that the volume ratio of said liquefied normally gaseous hydrocarbon to said second bottoms fraction is about 5:1.

8. A process for treating a residual oil containing to an elevated temperature in the range 750–1000° F. asphaltic constituents which comprises heating said oil under mild vis-breaking conditions, fractionating the resulting vis-broken oil to yield a first gas oil fraction and a first bottoms fraction, fractionating said first bottoms fraction to produce a second gas oil fraction and a second bottoms fraction, fractionating said first gas oil fraction to separate therefrom hydrocarbons having a boiling point not greater than 500° F. and to yield a third bottoms fraction, subjecting said second bottoms fraction to liquid-liquid contact with a liquid deasphalting solvent comprised of a major amount of a C_4 paraffinic hydrocarbon under deasphalting conditions to separate asphaltic constituents from said second bottoms fraction and to yield a deasphalted oil fraction, combining said third bottoms fraction, said second gas oil fraction and said deasphalted oil fraction, subjecting the result-

ing combined fractions to liquid-liquid solvent refining in contact with furfural in the presence of a light paraffinic hydrocarbon suitable for use as a deasphalting solvent, recovering from the aforesaid furfural solvent refining operation a raffinate having a reduced amount of more aromatic hydrocarbons and a lowered metals content relative to said resulting combined fractions and an extract having an increased amount of relatively more aromatic hydrocarbons relative to said resulting combined fractions and said raffinate, combining said raffinate and said hydrocarbons having a boiling point not greater than about 500° F., subjecting the resulting combined stream to catalytic cracking, separating from the resulting catalytic cracked effluent a cracked gas oil fraction, recovering said asphaltic constituents separated during said deasphalting operation, adding a portion of said extract and said cracked gas oil fraction to said recovered asphaltic constituents, fractionating the resulting admixture containing said asphaltic constituents to separate therefrom said C_4 paraffinic hydrocarbons deasphalting solvent and admixing additional said extract and said cracked gas oil fraction with the resulting asphaltic constituents now substantially free of deasphalting solvent.

9. A process in accordance with claim 8 wherein said deasphalted oil fraction subjected to furfural solvent refining contains admixed therewith C_4 paraffinic hydrocarbon deasphalting solvent.

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