

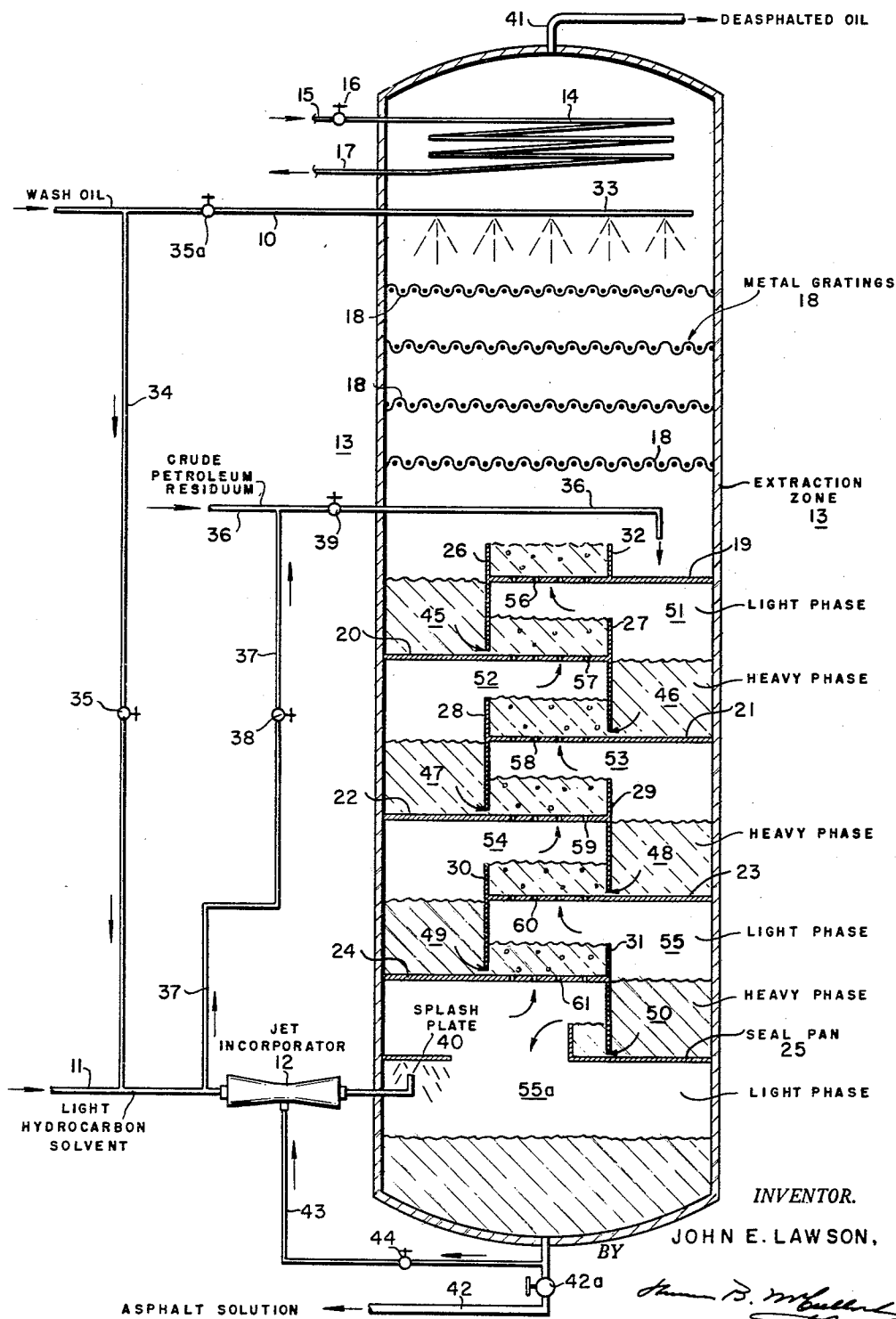
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EXTRACTION OF RESIDUUM

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EXTRACTION OF RESIDUUM

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The present invention is directed to the extraction of crude petroleum residuum. More particularly, the invention is concerned with the extraction of crude petroleum residuum employing a liquefied, normally gaseous, hydrocarbon solvent. In its more specific aspects, the invention is directed to recovering increased yields of deasphalted oil from crude petroleum residuum by extraction of the crude petroleum residuum with a liquefied, normally gaseous hydrocarbon solvent.

The present invention may be briefly described as the extraction of a crude petroleum residuum which contains asphalt constituents and oil with a liquefied, normally gaseous hydrocarbon solvent in which a solution of the residuum in the solvent is introduced into an elongated, vertical extraction zone at an upper level thereof. The solvent is introduced into the extraction zone at a lower level thereof and the solvent and solution are maintained in said zone under extraction conditions of temperature and pressure. The solvent and solution are flowed counter-currently in said zone and at least a light phase and at least a heavy phase are formed in said zone between the upper level and the lower level. The light phase which comprises solvent and oil is dispersed in the heavy phase which comprises asphalt and solvent. Thereafter there are recovered from said zone asphalt-free oil and an asphalt constituent phase.

The liquefied, normally gaseous hydrocarbon solvent may be propane and/or butane with small amounts of heavier and lighter constituents. The liquefied, normally gaseous hydrocarbon may also include propylene and the butylenes. A satisfactory solvent may comprise about 66 percent of C_3 hydrocarbons and a small amount of lighter materials and about 34 percent of C_4 hydrocarbons, including a small amount of heavier materials. The solvent may satisfactorily be either propane and the butanes or may contain propylene and propane and the butylenes and butanes. The amount of material lighter than the C_3 hydrocarbons may be of the order of about 1.5 percent by volume while the amount of heavier material than the C_4 hydrocarbons may be no greater than about 1 percent by volume. Satisfactory operations are obtained with a mixture comprising about 60–63 percent propane and/or propylene and about 29–32 percent of butanes and/or butylenes with the remainder being some lighter and heavier material.

The extraction temperatures may range from about 100° to about 250° F. while pressures will be sufficient to maintain a liquid phase. In other words, a pressure may be employed in excess of the vapor pressure of the solvent at the operating temperature.

The light phase of the present invention is predominantly solvent and oil and may have a density of about 0.4 to about 0.6 while the heavy phase is predominantly asphalt constituents and solvent and may have a density from about 0.7 to 0.9.

In the practice of the present invention, the residuum may be diluted with about .2 to about .5 volume of

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solvent per volume of residuum to form the solution which is introduced into the extraction zone.

The amount of liquefied, normally gaseous hydrocarbon solvent may suitably be in the range from about three volumes to about ten volumes per volume of residuum.

The ratio of light phase to heavy phase may be in the range from about 3 to 30 to 1 with satisfactory results being obtained at a ratio of light phase to heavy phase of about 7 to 1.

It is contemplated that, in the practice of the present invention, a heavy wash oil may be introduced into the extraction zone at a point above the point where the residuum solution is introduced and the wash oil may also be introduced along with the hydrocarbon solvent. The amount of solvent-free wash oil introduced into the extraction zone may be in the range from about 0.05 to 0.20 volume per volume of crude petroleum residuum. A suitable wash oil may be obtained from crude petroleum from the Hawkins Field in Texas or may be a catalytic tar or a heavy fraction such as described in U.S. Patents 2,793,168 and 2,777,802. Other wash oils suitable in the practice of the present invention are described in Serial No. 493,371, filed March 10, 1955, now U.S. Pat. No. 2,853,426, for Nick P. Peet.

The present invention will be further illustrated by reference to the drawing in which the sole figure is an elevational view in section of an extraction zone for practice of a preferred mode.

Referring now to the drawing, numeral 11 designates a charge line by way of which a light hydrocarbon solvent comprising a major amount of propane and a minor amount of butanes is introduced into the system from a source not shown. Line 11 leads into a jet incorporator 12 and from thence into a vertical, elongated extraction zone 13. Vertical elongated extraction zone 13 is provided with a steam coil 14 in its upper end, into which steam is introduced by way of line 15, controlled by valve 16, and this exhaust steam is discharged by way of line 17. A plurality of steam coils may be used as may be required.

Vertical elongated extraction zone 13 may be provided with a plurality of vertically spaced apart expanded metal gratings 18 and is also provided with perforated trays 19, 20, 21, 22, 23, and 24, as well as with a seal pan 25. The trays 19, 20, 21, 22, 23, and 24 are vertically spaced apart and are provided with vertical members 26, 27, 28, 29, 30, and 31 as illustrated which form a plurality of weirs; plate 19 is provided with a weir 32 to isolate a portion of the plate 19 for introduction of the solution as will be described. The vertical member 31 forms a seal with the seal pan 25 as has been illustrated.

The plates 26, 27, 28, 29, 30, and 31 are arranged to provide flow as will be described.

The plates 19–24 inclusive are perforated for upward flow through the plates in a manner which will be described.

Extraction zone 13 is also provided with a line 10 which leads into a spray 33 by way of which a heavy wash oil is introduced into the system. Line 10 connects with line 11 by way of branch line 34 to allow wash oil to be introduced with the solvent through line 11. Flow ratio through line 10 and 35 are controlled by valves 35a and 34, respectively.

Crude petroleum residuum is introduced into the system through line 36 and has admixed with it solvent introduced from line 11 from branch line 37 controlled by valve 38, line 36 being controlled by valve 39 and introducing the solution of crude petroleum residuum into the extraction zone onto plate 19 as shown.

Line 11 which contains jet 12 introduces solution into

zone 13 below a suitable splash plate 40 as shown in the drawing.

Deasphalted oil in solution in the solvent is withdrawn from zone 13 by way of line 41 and may be further treated for removal of metal contaminants as described in U.S. Patent 2,793,168 and removal of solvent by a suitable means. Asphalt is discharged in solution by way of line 42 controlled by valve 42a for further treatment for recovery of solvent.

A branch line 43 controlled by valve 44 is provided for introducing as may be desired a portion of the asphalt solution withdrawn by line 42 into jet 12 for recycling to zone 13 with the solvent introduced by line 11.

By virtue of the arrangement of plates 19-24 inclusive and the vertical members 26-31 inclusive and by virtue of the flow through the extraction zone 13, there is formed on the several plates a plurality of heavy phases 45, 46, 47, 48, 49, and 50, and a plurality of light phases 51, 52, 53, 54, 55, and 55a with the light phases 51-55a inclusive being introduced into an adjacent heavy phase through the perforations 56, 57, 58, 59, 60, and 61 in plates 19, 20, 21, 22, 23, and 24, respectively, as illustrated. By virtue of dispersing a light phase into an adjacent heavy phase in the practice of the present invention, it is possible to increase the yields of deasphalted oil in a substantial and unexpected manner. This comparison is drawn with normal practice wherein heavy phase dispersed in the light phase comprises the flow regime. Dispersion of the light phase, which may be four to twenty times greater in volume, into the heavy phase causes a greater interfacial area to be created, thus giving rise to a greater opportunity for mass transfer which results in higher contacting efficiency. The light phase has a much lower viscosity and therefore greater mobility than the heavy phase. This factor gives rise to greater circulation within droplets of the light phase as compared to heavy phase droplets which results in higher mass transfer coefficients, also increasing efficiency of contacting. This results in improved extraction efficiency and

considerable operational advantages in deasphalting operations. For example, control of phase interface on each tray is positive. Also contacting intensity may be controlled to any desired level by varying design features of the perforated trays and improved yields of deasphalted oil are obtained. Additionally, an asphalt of a greater specific gravity is obtained over that normally obtainable by virtue of recovering increased yields of deasphalted oil.

In order to illustrate the invention further, comparative extractions were made on a crude petroleum residuum containing asphalt and oil. The following table compares operations with the present invention as compared to an operation where the heavy or asphalt phase was dispersed into the solvent phase. The following table summarizes operating conditions and yields with the first column showing the invention and second column the conventional operation.

TABLE I
Barrels per day

	1	2
Charge, b./d. (Corrected to 60° F.)	11,300	11,760
Solvent Circulation, b./d.		
To Tower	46,600	46,500
Predilution	4,290	5,300
Deasphalted Oil, b./d.	6,060	4,350
Wash Oil Rate, b./d.	660	660
Yield, Volume Percent	53.6	37.0
Tower Temperatures, °F.:		
Top	175	174
Bottom	170	170
Flux to Asphalt, b./d.	1,550	1,500
Fluxed Asphalt, b./d.	7,450	9,570
Solvent/Residuum, Ratio, Total	4.5	4.41

From the foregoing Table I, it will be seen from the data in column 1 representing the present invention that a yield of deasphalted oil greatly in excess of that obtainable in the conventional operation was obtained. It will be noted that all conditions were substantially identi-

TABLE II

	Re-siduum Charge	1					2				
		Deasphalted Oil	Asphalt	Fluxed Asphalt	Flux	Wash Oil	Deasphalted Oil	Asphalt	Fluxed Asphalt	Flux	Wash Oil
Specific Gravity ¹	0.9910	0.9441	1.0333			1.0430	0.9463	1.0175			1.0212
°API	11.5	18.7	4.5	10.3	36.1	5.6	18.6	7.8	12.0	34.0	8.5
Conradson Carbon ¹	14.23	3.67	23.7			13.0	3.87	18.4			9.65
Sulfur, Wt. Percent ¹	2.40	1.33	3.11	3.52	0.287	1.45	1.28	2.69	2.34	3.39	1.33
Aniline Point		222					221				
Nitrogen	0.31	0.134					0.12				
Pour, ° F.		85		45			95		40		
Nd at 67° F.		1.5102					1.5121				
Wet Ash, p.p.m. ¹ :											
Ni	23.6	0.99	29.9			<0.2	0.86	24.8			<0.2
V	33.0	0.48	54.5			<0.3	0.34	43.8			<0.3
Fe	35.6	0.52	55.1			3.35	0.60	42.0			5.25
SSU at 210° F.		217				103.2	197.5				74.8
SSU at 275° F.	424	79.1		275			75.3		176.7		
SSF at 210° F.	228			99.6		15.5			65.1		13.0
SSF			370					131.3			
Agg. Ash ¹	0.0277	0.00192				0.0185	0.00259				0.0383
Water Sol. Ash				0.03	0.002				0.011	0.0008	
Flash, P.M.				188	176				215	180	
Explosivity, Percent				35.0	18.0			7.0	10.0	10.0	
Molecular Wt. ¹		787					803				
Bromine Number		8.0					8.8				
Total Ash			0.05	0.045	0.0060	0.017		0.039	0.033		
ASTM Dist.:											
IBP		77% off at 1,132			362	95.5% off at 1,132	76% off at 1,132			390	48% off at 1,132
FBP					596					611	
5%		846			404	748	829			425	753
10%		898			411	766	899			436	790
20%		966			424	790	953			448	841
30%		1,000			434	840	1,000			458	894
40%		1,027			445	867	1,030			468	944
50%		1,057			456	888	1,058			477	
60%		1,082			466	913	1,084			488	
70%		1,109			470	937	1,110			499	
80%					494	971				512	
90%					517	1,021				529	
95%					638	1,108				552	

¹ Average of at least two determinations.

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cal as close as could be obtained in a commercial operation.

Further to show the improvement of the present invention, the following inspection characteristics are shown in Table II wherein the data under 1 shows the present invention; wherein the data under 2 shows the comparative operation not utilizing the present invention. Characteristics of the flux and wash oil are also shown. Also, the fluxed asphalt characteristics from the two operations are also presented.

It may be seen from the inspection in Table II that the deasphalted oil from the two operations were substantially identical in quality but yet increased yields of deasphalted oil were obtained in accordance with the present invention, which shows that at a constant yield, improved quality deasphalted oil with a lowered metal content is obtainable. This is quite important and useful in preparing feeds for cracking operations, and the like.

It is noted that the asphalt obtained in the present invention is considerably heavier than the asphalt from the comparative run, showing that greater quantities of the deasphalted oil have been recovered.

Attention is especially directed to the lowered Conradson carbon of the deasphalted oil in the practice of the present invention over that obtained in the comparative operation.

From the foregoing runs, it may be concluded that the present invention allows obtaining of substantially improved results in that greater yields of deasphalted oil are obtainable than was possible heretofore without a sacrifice in quality. In other words, it is now possible to recover deasphalted oil in substantially improved yields for use as a catalytic cracking feedstock as may be desired.

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

1. A method for extracting a residuum fraction to obtain a substantially asphalt-free oil which comprises forming a solution of a crude petroleum residuum containing asphalt constituents and oil in a liquefied normally gaseous hydrocarbon solvent, introducing said solution into an elongated vertical extraction zone at an upper level thereof, introducing said solvent into said zone at a lower level thereof, said solution and solvent being maintained in said zone under extraction conditions including a temperature between 100° and 250° F. and pressure sufficient to maintain a liquid phase, flowing countercurrently in said zone said solvent and solution, forming in said zone at least a light phase comprising predominantly said solvent and said oil, forming in said zone at least a heavy phase comprising predominantly said asphalt constituents and solvent, dispersing said light phase into said heavy phase, said light phase and heavy phase being in a ratio in the range from about 3 to 30:1, and said light phase having a density of about 0.4 to about 0.6 and said heavy phase having a density of about 0.7 to 0.9, and recovering from said zone increased yields of substantially asphalt-free oil and an asphalt constituent phase.

2. A method in accordance with claim 1 in which a heavy wash oil is introduced into said zone above said solution.

3. A method in accordance with claim 1 in which the solvent comprises predominantly C₃ and C₄ hydrocarbons.

4. A method for extracting a residuum fraction to obtain a substantially asphalt-free oil which comprises forming a solution of a crude petroleum residuum containing asphalt constituents and oil in a liquefied normally gaseous hydrocarbon solvent having from 3 to 4 carbon atoms in the molecule, introducing said solution into an elongated vertical extraction zone at an upper level thereof, introducing said solvent into said zone at a

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lower level thereof, said solution and solvent being maintained in said zone under extraction conditions including a temperature in the range between 100° and 250° F. and pressure sufficient to maintain a liquid phase, flowing countercurrently in said zone said solvent and solution, forming in said zone at least a light phase comprising predominantly said solvent and said oil, forming in said zone at least a heavy phase comprising predominantly asphalt constituents and solvent, said light and heavy phases being formed between said upper level and said lower level in said zone, dispersing said light phase into said heavy phase, said light phase and heavy phase being in a ratio in the range from about 3 to 30:1, and said light phase having a density of about 0.4 to about 0.6 and said heavy phase having a density of about 0.7 to 0.9, and recovering from said zone increased yields of substantially asphalt-free oil and an asphalt constituent phase.

5. A method in accordance with claim 4 in which a portion of the asphalt constituent phase is recycled to said zone in admixture with said solvent.

6. A method in accordance with claim 4 in which a heavy wash oil is introduced into said zone above said solution.

7. A method for extracting a residuum fraction to obtain a substantially asphalt-free oil which comprises forming a solution of a crude petroleum residuum containing asphalt constituents and oil in a liquefied normally gaseous hydrocarbon solvent, introducing said solution into an elongated vertical extraction zone at an upper level thereof, introducing said solvent into said zone at a lower level thereof, said solution and solvent being maintained in said zone under extraction conditions including a temperature between 100° and 250° F. and pressure sufficient to maintain a liquid phase, flowing countercurrently in said zone said solvent and solution, forming in said zone a plurality of light phases comprising predominantly said solvent and said oil, forming in said zone a plurality of heavy phases comprising predominantly asphalt constituents and solvent, said light and heavy phases being formed between said upper level and said lower level in said zone with a light phase adjacent a heavy phase, dispersing each light phase into its adjacent heavy phase, said light phases and said heavy phases being in a ratio in the range from about 3 to 30:1, and said light phase having a density of about 0.4 to about 0.6 and said heavy phase having a density of about 0.7 to 0.9, and recovering from said zone increased yields of substantially asphalt-free oil and an asphalt constituent phase.

8. A method for extracting a residuum fraction to obtain a substantially asphalt-free oil which comprises forming a solution of a crude petroleum residuum containing asphalt constituents and oil in a liquefied normally gaseous hydrocarbon solvent having from 3 to 4 carbon atoms in the molecule introducing said solution into an elongated vertical extraction zone at an upper level thereof, introducing said solvent into said zone at a lower level thereof, introducing a heavy wash oil into said zone at a point above the introduction of said solution, said solution and solvent being maintained in said zone under extraction conditions including a temperature between 100° and 250° F. and pressure sufficient to maintain a liquid phase, flowing countercurrently in said zone said solvent and solution, forming in said zone at least a light phase comprising predominantly said solvent and said oil, forming in said zone at least a heavy phase comprising predominantly asphalt constituents and solvent, said light and heavy phases being formed between said upper level and said lower level in said zone, dispersing said light phase into said heavy phase, said light phase and heavy phase being in a ratio in the range from about 3 to 30:1, and said light phase having a density of about 0.4 to about 0.6 and said heavy phase

having a density of about 0.7 to 0.9, recovering from said zone increased yields of substantially asphalt-free oil and an asphalt constituent phase, and recycling a portion of the asphalt constituent phase to said zone in admixture with said solvent.

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