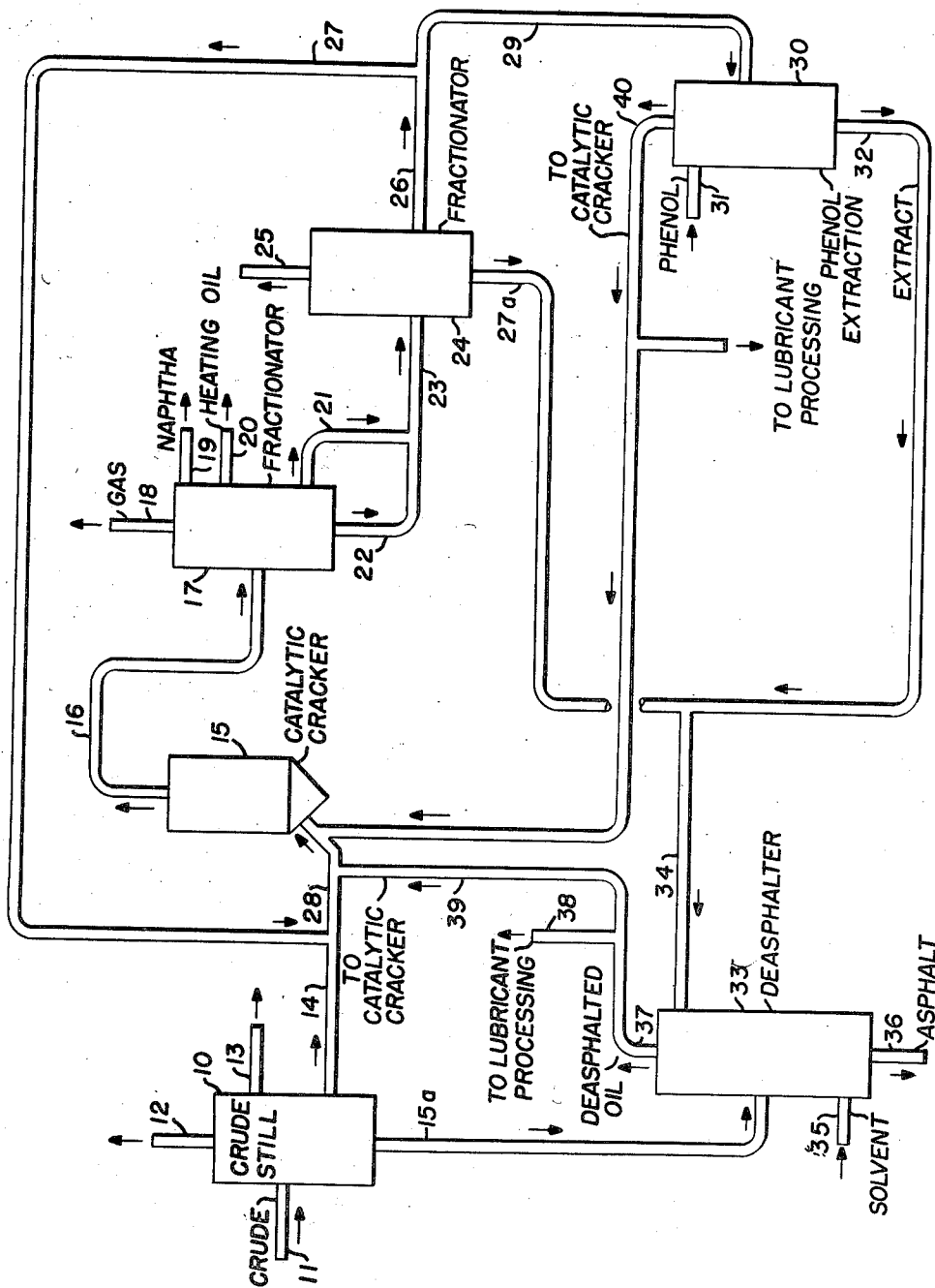


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 INTEGRATED PROCESS FOR MANUFACTURE OF GASOLINE
 AND LUBRICATING OILS
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INTEGRATED PROCESS FOR MANUFACTURE OF GASOLINE AND LUBRICATING OILS

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This invention relates to a method of processing crude oil, and more particularly to a method of processing the higher boiling components of crude oil for the manufacture of gasoline and lubricating oil.

The increasing demand for gasoline and lubricating oil has made it desirable to develop processes for obtaining the maximum yield of these high quality products while at the same time minimizing the yield of less valuable heavy constituents such as fuel oil. In such processes it has been desirable to feed a hydrocarbon fraction, usually boiling in the range of about 500°–1200° F., into a cracking step, preferably a catalytic cracking step. Such cracking operations serve to produce gasoline and a so-called "catalytic cycle stock" which contain from about 20 to 70% of aromatic hydrocarbons, mostly condensed ring compounds. In the manufacture of high quality lubricating oil by the phenol extraction of such a mixture, these aromatic compounds, which are more concentrated in the lower and higher boiling fractions of the hydrocarbon mixture, are essentially 100% soluble in phenol, and inclusion of these fractions in the feed to the phenol extraction unit serves to decrease the selectivity of the phenol and to increase the solvent requirements of the process. It has been found that by a suitable fractionating technique such "cycle" stocks may be segregated into a fraction relatively rich in aromatic constituents and a fraction relatively poor in aromatic constituents. The fraction relatively poor in aromatics may advantageously be used as feed for a phenol extraction process for the manufacture of high quality lubricating oil or catalytic cracking feed. It has been further found that the higher boiling portion of the fraction relatively rich in aromatic hydrocarbons is useful as a wash material in conjunction with the deasphalting of crude residuum or for other special uses. The addition of highly aromatic material results in the precipitation of various metallic constituents and thus enables the production of deasphalted oil of very low metallic ash content.

It is an object of the present invention to provide an integrated process for the treatment of crude oil in which the steps of distillation, cracking, extraction, and deasphalting are integrated to minimize the yield of fuel oil and to maximize the yields of high quality products such as lubricating oil and gasoline.

It is a further object of the present invention to provide an integrated process for the treatment of crude oil, including a solvent extraction step wherein a feed stock relatively low in aromatic content is provided for such solvent extraction step.

It is yet another object of the present invention to provide a process whereby a deasphalted oil having a low metallic ash content may be produced from a residual stock.

These and other objects of the invention, which will be in part apparent and in part specifically pointed out in the subsequent description, are attained by providing a process for the treatment of crude oil comprising the

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steps of distilling crude petroleum oil to obtain a virgin hydrocarbon fraction boiling within the range of 500°–1200° F. and a bottoms fraction. The distillate fraction is then catalytically cracked and the cracked products boiling above about 600° F. are segregated into one fraction relatively rich in aromatic hydrocarbons and a second fraction relatively poor in aromatic hydrocarbons. The bottoms fraction from the crude oil distillation operation is then washed with the hydrocarbon fraction relatively rich in aromatic material, in conjunction with a deasphalting process, to produce a hydrocarbon mixture of low metallic ash content suitable as a cracking feed stock or the manufacture of high viscosity lubricating oils.

The process of the present invention may be better understood by reference to the accompanying single figure of drawings, which illustrates schematically a preferred embodiment of the process of the present invention.

Turning now specifically to these drawings, there is illustrated a crude oil still 10, into which crude oil is fed through line 11. The still 10 is operated in a conventional manner to produce the usual light products, which are shown as being taken off overhead at 12 and 13, and a hydrocarbon fraction boiling in the range of 500°–1200° F., which is taken off through line 14. Higher boiling residual materials form a bottoms fraction, which is removed through line 15a.

The hydrocarbon fraction taken off at 14 is in the boiling range especially adapted to be used as feed for a catalytic cracking operation carried out in unit 15. The catalytic cracking unit 15 is operated under conditions which are conventional and well known to those skilled in the petroleum refining art, and which will therefore not be described in detail. This cracking unit may be of the fluid bed, moving bed or fixed bed type. The cracked products formed by this operation pass from the cracking unit 15 through line 16 to the fractionating tower 17. In the fractionator 17 the cracked products are separated into a gas fraction which is taken overhead at 18, a naphtha fraction which is taken off at 19, and a heating oil fraction which is taken off through line 20. A relatively heavy side stream boiling in the range of about 600°–900° F., is taken off through line 21 and is mixed with the bottoms which leave the fractionator through line 22. These combined streams form a hydrocarbon mixture boiling in approximately the same range as the virgin feed to the catalytic cracking operation, i. e., about 600°–1200° F. The cracked mixture then enters second fractionator 24. A function of the fractionator 24 is to separate the cracked hydrocarbons according to the aromatic content thereof. It has been found that in such a mixture the highest boiling 10–30% by volume is extremely aromatic, being in the order of 75–90% aromatic rings. The lowest boiling 10–30% may consist of compounds as high as 60–70% aromatic rings. It is this highly aromatic material, which is very highly soluble in phenol, which it is desired to separate prior to a phenol extracting treatment of the cracked material for the purpose of manufacturing high quality lubricating oil. In operating the fractionator it is preferred to take off overhead through line 25 all of the components boiling below about 650°–700° F. This overhead cut will vary from about 5% to 30% by volume on the feed, depending upon the fractionation obtained in the first fractionator 17. About 20% to 80% of the feed amounts to hydrocarbon mixture boiling in the range of about 700°–1100° F., which is taken off as a side stream through line 26. The high boiling bottoms cut will contain from 60% to 90% aromatic constituents based on the average percentage of aromatic rings in each molecule. Normally this bottoms fraction which is taken

off through line 27 will vary between 5% and 30% of the feed to the fractionator 24.

The fraction of relatively low aromatic content taken off at side stream 26 provides excellent catalytic cycle stock and may be totally or partially recycled via line 27 to mix with the virgin feed from line 14 at 28 and be returned to the catalytic cracking operation 15. Preferably, however, a major portion of this side stream is fed through line 29 to the phenol extraction tower 30. Phenol is introduced at the top of the tower through line 31 and extracts aromatic constituents from the hydrocarbon mixture. Due to the relatively low aromatic content of the feed material to the extraction unit 30, a relatively small volume of phenol may be employed. This volume depends, of course, upon the use to which the raffinate phase is to be put. If a high quality lube oil is to be produced, 75–200% by volume of phenol will be required, whereas if this stock is extracted to provide a cracking feed, it is necessary to remove only the more highly condensed ring aromatics. For this purpose, 40–100% by volume of phenol is adequate. It will be appreciated that this ratio of phenol to feed stock is appreciably lower than that normally employed. Since most phenol plants are limited by solvent recovery capacity, the capacity of any given extraction unit is greatly increased by employment of the process described. As will be seen from a subsequent example, comparable results may be obtained employing 40% less phenol when separation of the more highly aromatic fraction is effected prior to extraction. Under such conditions, the capacity of a given phenol extraction unit for producing a given quality raffinate would be increased by about 67% using the same volume of phenol.

The highly aromatic extract phase leaves the extraction unit 30 through line 32, and after suitable separation of solvent the highly aromatic hydrocarbon mixture may be combined with the aromatic bottoms leaving fractionator 24 via line 27a and this mixture is fed into a propane deasphalting unit 33 via line 34. Alternatively, these streams may be fed separately to the deasphalting unit. The feed stock for the deasphalting unit 33 is provided by the crude residuum which leaves the still 10 via line 15a. Liquid propane is introduced into the unit at 35 and deasphalting is carried out in the conventional manner. The addition of propane precipitates the asphalt content of the crude residuum, whereas the addition of the aromatic hydrocarbons via line 34 effects a precipitation of metallic constituents such as salts of iron, nickel, vanadium, etc. These precipitate with the asphalt and are removed at the bottom of the deasphalting tower through line 36. The use of the highly aromatic wash oil also serves to reduce the Conradson carbon value of the deasphalted oil.

Aromatics boiling above about 600° F. are effective wash solvents in this washing process but lower boiling aromatics, such as those boiling in the range of 600 to 950–1000° F. are soluble to varying degrees in propane and other deasphalting solvents and are consequently carried into the deasphalted oil stream. Where such aromatics are objectionable in the deasphalted oil, the wash solvent should be topped to provide a wash oil having an initial boiling point of about 950–1000° F.

The deasphalted oil is taken off through line 37 and the propane is recovered by conventional means not shown. All or a portion of the deasphalted oil may be removed via line 38 and used as a feed stock for the manufacture of lubricating oil, or it may be passed to the catalytic cracking unit 15 via line 39. The absence of metallic salts which serve to poison the cracking catalyst and the relatively low Conradson carbon value make this oil particularly desirable for the latter purpose.

The raffinate phase from the phenol extraction unit 30 is removed via line 40 and the phenol recovered by conventional means not shown. The dephenolized raffinate may then be subjected to various finishing procedures such

as dewaxing and decolorizing to produce a finished lubricating oil. If desired, all or a portion of the raffinate may be recycled through line 40 to the catalytic cracking unit 15. Alternatively, the highly aromatic bottoms from fractionator 24 and the extract phase from the phenol extraction unit 30 may be desulfurized instead of being used in the deasphalting process, and the desulfurized product may be useful as a highly aromatic low sulfur fuel.

Example I

The following example illustrates this procedure. A virgin distillate of 21.3 API gravity, 650° F. initial boiling point, 960° F. mid boiling point, 18% aromatic ring and 30% naphthenic ring content was subjected to fluid cracking. The cycle stock boiling above 650° F. was fractionally distilled into 10% cuts having the following inspections.

Cut	API Gravity	Mid boiling Point, °F.	Percent Aromatic Rings	Percent Naphthenic Rings
Total Cycle Stock.....	16.5	901	43.8	10
0-10.....	15.3	718	47.5	8.5
10-20.....	15.6	769	45.1	12.3
20-30.....	16.2	817	37.2	14.8
30-40.....	17.7	843	34.1	15.6
40-50.....	18.4	876	31.7	16.9
50-60.....	19.5	915	28.9	14.8
60-70.....	20.6	940	24.7	14.1
70-80.....	20.1	973	23.2	13.7
80-90.....	11.4	1,032	57.8	11.6
90-100.....	-1.9	1,070	90+	-----

It is apparent that by eliminating the fractions boiling below about 817° F. and above about 973° F. that a stock of substantially reduced aromaticity is formed. The cuts of lower aromaticity and having mid boiling points of 817° F.–973° F., representing a 20–80% fraction by volume on the total cycle stock were blended together and this product was extracted with phenol, as was the total cycle stock. The results of these extractions are given below.

	Total Cycle Stock	20-80% Cut As Cycle Stock
Percent Phenol.....	100	60
Raffinate Yield Percent on Feed.....	54	67

	Feed Stock	Raffinate	Feed Stock	Raffinate
Product Inspections:				
A. P. I. Gravity.....	16.5	31.2	18.8	32.3
Percent Aromatic Rings.....	43.8	8.7	29.9	7.9
Percent Naphthenic Rings.....	10	17.3	14.9	21.2

These results clearly demonstrate that the total cycle stock boiling in approximately the same range as the feed stock can be separated into two fractions by distillation to give two products, one appreciably lower in aromatics than the total cycle stock and the other appreciably higher. Solvent extraction of the cut low in aromatics gives a higher yield with lower solvent requirements and similar raffinate quality as compared with extraction of the total cycle stock. By eliminating the most highly aromatic fractions prior to extraction, substantial reductions of phenol requirements are obtained.

Example II

The following example illustrates the use of the high boiling condensed ring aromatics as a wash oil in deasphalting a residual stock to obtain a low carbon, low metal content deasphalted oil. The 20% bottom obtained by distilling the total cycle stock in the previous example was used as a wash oil introduced near the top

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of the deasphalting tower. This product had a specific gravity of 1.0508, a mid boiling point of 1052° F., and contained 78% of aromatics. Deasphalting conditions and product inspections are summarized below.

Volume Percent Wash Oil.....	0	20
Volume Percent Solvent (65% C ₃ -35% C ₄).....	500	500
Tower Top Temperature, °F.....	180	180
Tower Bottom Temperature, °F.....	160	160
Deasphalted Oil Yield, Percent.....	52.5	54.7

	Residual Feed	Deasphalted Oil	
Product Inspections:			
Specific Gravity.....	1.01	.946	.949
Percent Carbon.....	16.6	3.8	3.0
Ni, p.p.m.....	25.0	1.6	0.8
V, p.p.m.....	37.4	1.9	0.9
Fe, p.p.m.....	19.6	3.2	1.1

These results show that the use of the wash oil in conjunction with deasphalting increased the yield of deasphalted oil and improved its quality as regards Conradson carbon and metal content. The deasphalted oil was of satisfactory quality for catalytic cracking feed or for the manufacture of lubricating oil of high quality.

In these experiments, a mixture of approximately 2/3 propane and 1/3 butane by volume was employed as the deasphalting solvent. Substantially pure propane or butane or any mixture of the two could be employed, depending on the yield of deasphalted oil and the quality desired. Increasing the propane content of the solvent or decreasing the deasphalting temperature serves to increase deasphalting yield. The quantity of solvent employed may vary from 100-1000% based on the residual feed. Increasing the solvent quantity serves to improve selectivity and deasphalted oil quality and/or deasphalted oil yield.

The quantity of aromatic wash oil may be varied from 5% to 50% on residual feed, improved deasphalted oil quality being obtained with increased quantities of wash oil. However, the advantage for using more than 30-40% of wash oil is limited.

In a countercurrent tower operation, the wash oil is introduced above the point of feed injection but below the tower top where deasphalted oil is withdrawn.

Although the present invention has been described with respect to an aspect using phenol as a selective solvent for aromatic hydrocarbons, it will be understood, of course, that the use of well-known equivalent solvents is contemplated and is within the purview of the invention. Examples of such selective solvents are furfural, nitrobenzene, and liquid sulfur dioxide.

While there has been described above a specific embodiment of the present invention together with a number of alternative procedures applicable thereto, it is to be understood that the invention is not to be limited thereby, but that it includes those equivalents which will occur to those skilled in the art.

What is claimed is:

1. A process of treating crude oil comprising the steps of distilling said crude oil to obtain a hydrocarbon fraction boiling within the range of about 500°-1200° F. and a bottoms fraction, cracking said hydrocarbon fraction, fractionating the cracked products to obtain a cracked fraction boiling in the same range as the first-named fraction, segregating the cracked fraction boiling in the same range as the first named fraction by distillation into a fraction relatively rich in aromatic hydrocarbons and a fraction relatively poor in aromatic hydrocarbons, and extracting said fraction relatively poor in aromatic compounds with a selective solvent to obtain a product substantially free of condensed ring aromatic compounds.

2. The process according to claim 1 wherein at least

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a portion of said fraction relatively poor in aromatic hydrocarbons is phenol extracted and the extract phase from such extraction is used in conjunction with a deasphalting solvent to wash metallic contaminants from said bottoms fraction.

3. The process of treating crude oil comprising the steps of distilling said crude oil to obtain a virgin hydrocarbon fraction boiling within the range of about 500°-1200° F. and a bottoms fraction, cracking said hydrocarbon fraction, fractionating the cracked hydrocarbon mixture so formed to produce a cracked hydrocarbon fraction boiling in the range of about 500°-1200° F., fractionating the last-named hydrocarbon fraction to obtain a fraction relatively rich in aromatic hydrocarbons and a fraction relatively poor in aromatic hydrocarbons, extracting at least a portion of said fraction relatively poor in aromatic hydrocarbons with phenol, and using the extract phase from such extraction in conjunction with said fraction relatively rich in aromatic hydrocarbons to wash metallic contaminants from said bottoms fraction.

4. The process according to claim 3 wherein the raffinate from said phenol extraction is dephenolized and subsequently converted to lubricating oil.

5. The process according to claim 3 wherein the washing of said bottoms fraction is carried out in conjunction with a light-hydrocarbon deasphalting operation.

6. The process of treating crude oil comprising the steps of distilling said crude oil to obtain a virgin hydrocarbon fraction boiling in the range of from about 500° F. to 1200° F. and a residual fraction, catalytically cracking said hydrocarbon fraction, fractionating the cracked hydrocarbon mixture so formed to produce a cracked hydrocarbon fraction boiling in the range of from about 500° F. to 1200° F., fractionating the last-named hydrocarbon fraction to obtain a bottoms fraction relatively rich in aromatic hydrocarbons amounting to about 20% by volume of the material fractionated, and a lighter fraction relatively poor in aromatic hydrocarbons, extracting at least a portion of said fraction relatively poor in aromatic hydrocarbons with phenol, introducing said residual fraction into a deasphalting zone, introducing liquefied, normally gaseous hydrocarbon solvent into said deasphalting zone, whereby said residual fraction is deasphalted to form a deasphalted phase which is washed with the combined extract phase and the fraction relatively rich in aromatic hydrocarbons.

7. Process according to claim 6 wherein said cracked hydrocarbon fraction is fractionated to obtain a high boiling cut and a low boiling cut relatively rich in aromatic hydrocarbons and an intermediate boiling cut relatively poor in aromatic hydrocarbons.

8. Process according to claim 7 wherein said low boiling fraction relatively rich in hydrocarbons amounts to about 20% by volume of the material fractionated and said high boiling fraction relatively rich in aromatic hydrocarbons amounts to about 20% by volume of the total material fractionated.

9. Process as defined by claim 6 wherein the extract phase from said extraction is combined with said fraction relatively rich in aromatic hydrocarbons prior to introducing the same into said deasphalting zone.

10. A process of claim 1 wherein said fraction relatively rich in aromatic hydrocarbons is used as a wash solvent in a light hydrocarbon deasphalting of a residual stock.

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