

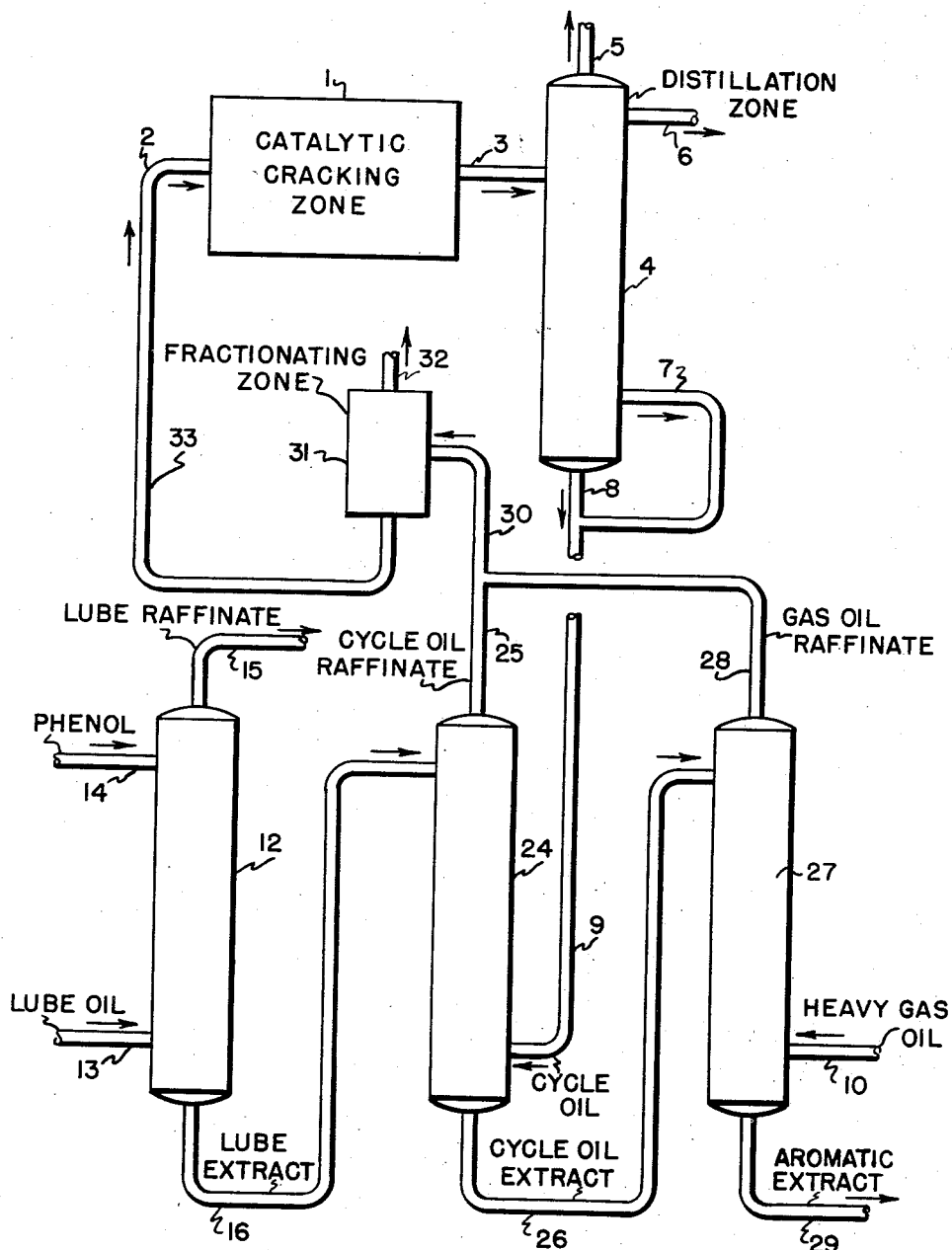
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COMBINATION CATALYTIC CRACKING PROCESS

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1

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COMBINATION CATALYTIC CRACKING PROCESS

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This invention relates to the refining of petroleum oils by a catalytic cracking operation. In one aspect, the invention provides a novel process for the upgrading of heavy products of a catalytic cracking operation so as to improve their relatively poor quality, thereby making them desirable for feed to catalytic cracking. In this regard, the cracking characteristics of catalytic cycle oil are improved materially by elimination of high molecular weight aromatic hydrocarbon types which are refractory to cracking. In another aspect, the invention includes a method for improving the value of a virgin gas oil fraction of a petroleum oil for catalytic cracking by substantially reducing or eliminating organic compounds containing metals that normally are present in the gas oil. Furthermore, the invention includes provision for improving the quality of the extract hydrocarbons obtained from extraction of a lubricating oil distillate, making these hydrocarbons more suitable for catalytic cracking.

The basic feature of this invention concerns the solvent extraction of virgin or cracked fractions of petroleum boiling in the gas oil boiling range so as to upgrade these fractions for use as catalytic cracking feed. The invention entails the use of selective solvents for aromatic hydrocarbons, employing these solvents to efficiently remove metal contaminants and refractory hydrocarbons from catalytic cracking feed stocks with substantially no loss of hydrocarbon constituents suitable for cracking. This is achieved by employing at least two extraction stages, in one of which cracked fractions of petroleum are treated and in the other of which virgin fractions of petroleum are treated. The heart of this invention entails the use of the total extract phase from one of these extraction stages for the treating or extraction agent in the other of the extraction stages. This innovation not only materially simplifies solvent recovery facilities but greatly improves the efficiency with which constituents are removed which are undesirable for catalytic cracking.

In its most specific and preferred form, the present invention accomplishes these objectives by integrating a lubricating oil extraction process with a catalytic cracking operation. In one embodiment of the invention, a lubricating oil is treated in an extraction operation with a selective solvent for aromatic hydrocarbons. The total extract phase formed in this extraction step is then used to contact catalytic cycle oil providing a first raffinate product. The total extract phase from this extraction of catalytic cycle oil is then employed to contact a gas oil which has undesired organic compounds containing metal contaminants providing a second raffinate product. The combined raffinate products resulting from these treatments include substantially all of the desirable constituents of the lubricating oil extract, cycle oil, and gas oil which are suitable for catalytic cracking while minimizing inclusion of detrimental metal contaminants and refractory aromatic hydrocarbons. In another embodiment of this invention, the extract phase from extraction of a lubricating oil is used to contact gas oil. The extract phase resulting is then used to contact catalytic cycle

2

oil. The cycle oil and gas oil raffinate products are particularly suitable for cracking.

In these and other specific embodiments of the invention high molecular weight aromatic hydrocarbons present in the solvent extract phase of a prior contacting step, serve to alter the nature of the gas oil and cycle oil extraction so as to provide raffinate products of improved characteristics for catalytic cracking feed.

As indicated, the present invention comprises a relatively complicated combination of a variety of treating steps and refining processes. In order to lay a basis for fully understanding the nature and features of this invention, attention will be directed to several aspects of the field involved.

At the present time, the process of catalytic cracking is extensively employed for converting high boiling portions of a petroleum crude oil to lighter boiling, commercially valuable products including gasoline and heating oils. The feed stock to a catalytic cracking unit ordinarily constitutes portions of a petroleum crude oil boiling above the gasoline boiling range or boiling above about 430° F. It is economically desirable to include the highest boiling fraction of a petroleum crude oil attainable by the vacuum distillation of atmospheric reduced crude, and for this purpose, the feed to a catalytic cracking unit preferably includes constituents of the crude oil boiling up to about 1100° F., or higher. As used herein, the term "gas oil" is used to identify this portion of a crude oil boiling in the range of about 430° to 1100° F. or somewhat higher.

For some time it has been appreciated that inclusion of the higher boiling portions of a crude oil in catalytic cracking feed stock causes the objectionable introduction to the catalytic cracking zone of higher concentrations of organic compounds which contain certain metal contaminants. Among the organic metallic contaminants present in heavy gas oil compounds of nickel, vanadium and iron are particularly objectionable in poisoning the catalyst used during catalytic cracking so as to decrease the selectivity and life of this catalyst. Recognizing this problem, there have been many suggestions aimed at minimizing metal contamination of gas oils to catalytic cracking feed. In this connection, one possibility is that organic metal contaminants can be reduced by contacting the gas oil with a solvent such as phenol. The contacting of phenol and gas oil reduces these contaminants, but at an economically prohibitive cost. This results from the fact that the phenol acts as a selective solvent to remove aromatic constituents of the gas oil as well as the undesired compounds containing metal contaminants. As a result, phenol contacting of gas oil conducted to eliminate organic metal contaminants of the gas oil provides a raffinate product in undesirably low yields. The remainder of the gas oil is present in the extract phase from this contact together with the organic metal contaminants removed from the raffinate. From the standpoint of hydrocarbon types, it is desirable to use the extract portion of the gas oil for catalytic cracking feed as well as the raffinate portion. It is apparent therefore that this process does not provide the desired objective of selectively separating the organic metal contaminants from the gas oil usable as catalytic cracking feed.

A basic feature involved in the present invention is the discovery that a selective solvent for aromatic hydrocarbons can be used to selectively extract organic metal contaminants from a gas oil. This is achieved while avoiding extraction of the hydrocarbon constituents of gas oil which are desirable for use as catalytic cracking feed. This is made possible by inclusion of high molecular weight aromatic hydrocarbons in the selective solvent-gas oil extraction system. The included high molecular weight aromatic hydrocarbons serve to displace compo-

nents of the gas oil normally extracted by fresh solvent alone. Another feature of this invention is the discovery that these high molecular weight, aromatic hydrocarbons actually serve as a solvent for these organic metal constituents. Consequently, larger reduction of these contaminants is realized.

It has been found that the high molecular weight aromatic compounds present in the extract phase of a catalytic cycle oil extraction process or a lubricating oil extraction process are uniquely adapted to provide the above function. Consequently, one aspect of the present invention entails the contact of a heavy gas oil with a selective solvent in the presence of aromatic hydrocarbons obtained from heavy cycle oil derived from a catalytic cracking process or in the presence of aromatic hydrocarbons derived from a lubricating oil. It is a particular feature of this invention that the desired aromatic hydrocarbons are derived from cycle oil or lubricating oil by solvent extraction, using the extract phase resulting from this contact as a selective solvent for gas oil extraction with use of the resulting extract phase in subsequent extraction steps, if desired.

The principles of this invention are illustrated in the accompanying drawing, which illustrates in diagrammatical form a flow plan embodying a specific embodiment of the invention.

Referring to the drawing, the processing steps involved in the practice of this invention are illustrated. The numeral 1 designates a catalytic cracking zone. The operation conducted in zone 1 may constitute any desired type of catalytic cracking operation. Thus, the catalytic cracking may constitute the fixed bed type of cracking, moving bed type of cracking, or fluidized catalytic cracking. In each of these types of operation, any of the various well known cracking catalysts may be employed. Generally, such catalysts are the metal oxide types and preferably include silica-alumina, silica-magnesia, or silica-gel promoted with metal oxides which are adsorbed thereon. Typical cracking conditions are at temperatures in the range of about 750° to 1050° F., and pressures ranging from atmospheric to somewhat above atmospheric pressure. The catalytic agent employed is regenerated intermittently or continuously in order to restore or maintain the activity of the catalyst.

In accordance with this invention, a particular catalytic cracking feed stock as derived in the manner described hereinafter is introduced to catalytic cracking zone 1 through line 2. For the present, it is sufficient to note that the feed to catalytic cracking zone 1 generally includes the fraction of a crude oil boiling within the range of about 430° to 1100° F. or higher. For typical operation, catalytic cracking of this feed stock would result in conversion of about 50 to 60% boiling in the gasoline-boiling range.

The products of catalytic cracking are removed from the catalytic cracking zone through line 3 for introduction to a product fractionator 4. Distillation zone 4 may be operated to permit removal of gas and low boiling gasoline from the catalytically cracked products overhead through line 5. Higher boiling gasoline is removed through sidestream withdrawal 6, and heavier fractions of the catalytically cracked products from lower portions of the fractionator. For example, a fraction boiling above about 430° F. and boiling up to about 700° or 800° F. may be removed from the lower sidestream withdrawal 7. Heavy residual fractions of the catalytically cracked products are removed from the bottom of the fractionator through line 8. Bottoms withdrawal stream 8 will include the highest boiling constituents of the cracked products including hydrocarbons boiling up to about 1100° F. or somewhat higher. In the event that powdered catalyst is employed in the catalytic cracking zone 1, some catalyst will be entrained in the bottoms withdrawal. In this case the product of line 8 may be

subjected to a clarification or settling operation in order to segregate the hydrocarbons from cracking catalysts. The product of this operation is commonly called clarified oil and the stream of line 8 will be so designated herein.

The fractions of catalytically cracked products boiling above about 430° F. and including the clarified oil are conventionally called cycle oil and in the process illustrated include the streams of both lines 7 and 8. While the process of this invention can be employed by using either of the streams of lines 7 or 8, the invention preferably employs both of these products as combined in line 9 of the drawings and designated by the term "cycle oil."

It is well known that cycle oil of the character identified is more refractory than virgin catalytic cracking feed stocks of the same boiling range and consequently constitutes relatively poor catalytic cracking feed stock. Cycle oil particularly includes refractory, high molecular weight, aromatic hydrocarbons which, if recycled to a catalytic cracking operation, cause excessive formation of undesirable gas, coke and tar during catalytic cracking. The constituents of cycle oil which are particularly objectionable for cracking are high molecular weight, aromatic hydrocarbons. The aromatic hydrocarbons present in cycle oil include polynuclear aromatic hydrocarbons and condensed ring aromatic hydrocarbons. The condensed ring aromatic hydrocarbons are particularly undesirable for inclusion in catalytic cracking feed stock. As will be seen, the process of this invention provides a means for improving cycle oil for catalytic cracking by elimination of these undesirable aromatic hydrocarbon types.

In accordance with the illustrated embodiment of the invention, the cycle oil is contacted with the extract phase of a lubricating oil extraction process. This extract phase may be obtained from the process illustrated at the left of the drawing occurring in the extraction zone 12. In zone 12, a lubricating oil distillate constituting the fraction of a crude oil boiling in the range of about 500° to 1100° F. is contacted with a selective solvent adapted to selectively extract aromatic constituents of the lubricating oil. Phenol is one of the selective solvents which may be employed, although other solvents may be employed such as furfural, nitrobenzene, aniline, cresol, etc. Anti-solvents or solvent modifiers may be used and conventionally are used in conjunction with these solvents for the extraction of a lubricating oil. For example, in the case of phenol, about 1 to 15% or somewhat higher percentages of water are preferably mixed with the phenol or separately injected during extraction, to provide the best extraction results. It is to be understood therefore, that the lubricating oil extraction process conducted in zone 12 may constitute any desired type of selective solvent extraction operation. As diagrammatically illustrated, extraction can be conducted by introducing lubricating oil at the lower portion of the extraction zone through line 13. The selective solvent, such as phenol, is introduced into the top of the illustrated extraction zone through line 14. The phenol will move downwardly through the extraction zone counter-current to an upwardly moving stream of lubricating oil, permitting extraction of constituents of the lubricating oil by the phenol during this contact. Perforated plates, packing, etc., may be used in the tower to aid this contacting. Alternatively, the extraction zone may be a tank mixer-settler combination or a centrifugal extraction device. A raffinate phase may then be recovered from the uppermost portion of the tower and withdrawn through line 15, the product of which upon dewaxing constitutes a finished lubricant. The extract phase removed from the bottom of the tower through line 16 will include the spent phenol solvent together with the extracted virgin aromatic constituents of the lubricating oil.

In this extraction process, the solvent to oil ratio will ordinarily be between about 0.5 to 1 and 3 to 1. When employed phenol, or phenol-water mixtures as the selective solvent, a solvent to oil ratio of about 1 to 1 to 2 to 1 is particularly suitable. In the case of phenol extraction, the extract phase of line 16 will primarily constitute spent phenol including aromatic hydrocarbons extracted from the lubricating oil. In general, the extract phase, will constitute about 60 to 95% (preferably 75 to 85%) phenol and about 40 to 5% of hydrocarbons extracted from the lubricating oil. In addition, dependent on the amount of water injection, about 0 to 15% of water will be included in the extract phase.

This extract phase resulting from selective extraction of a gas oil to produce high quality lubricating oil is usually of value as a catalytic cracking feed stock. The extracted hydrocarbons for the most part constitute single nucleus aromatic hydrocarbons with substituted alkyl radicals which make the compounds sufficiently paraffinic so that they can be attractively subjected to cracking. In the past, after solvent removal, the extract hydrocarbons from a lubricating oil extraction process have been used as catalytic cracking feed. The solvent recovery operation is a processing step which requires extensive and expensive recovery facilities. It is one of the features of this invention to permit extraction of catalytic cycle oils without the addition of such expensive equipment by making use of the lubricating oil extraction process in a novel and inexpensive manner. This is achieved in accordance with this invention by employing the lubricating oil extract phase as the extraction agent for catalytic cycle oil. Incidental quality improvement is realized for lubricating oil extract as a catalytic cracking feed.

For this purpose, the total extract phase from the lubricating oil extraction is contacted with the cycle oil of line 9. This may be carried out in any kind of extraction zone which may be an extraction tower 24 similar in nature to extraction tower 12. Thus, the cycle oil will be introduced to a lowermost portion of tower 24 through line 9 while lubricating oil extract phase will be introduced to the top of tower 24 through line 16. Cycle oil will flow upwardly through the tower countercurrent to downwardly moving portions of the lubricating oil extract phase.

This contacting results in displacement of lubricating oil constituents from the phenol solvent by cycle oil constituents. In particular, it appears that condensed ring aromatic hydrocarbons present in the cycle oil are more soluble in the solvent than the extracted lube constituents in the lubricating oil extract phase. Therefore, these extract hydrocarbons are displaced from the phenol phase. It has been found that substantially all of the lubricating oil constituents can be recovered from the lube extract phase so as to be removable as a raffinate product from the top of tower 24 through line 25. This raffinate product will also include constituents of the cycle oil suitable for catalytic cracking.

The extract phase formed in tower 24 is removed as a bottoms product through line 26. This extract phase will include most of the phenol originally introduced to tower 12 through line 14 and will include aromatic hydrocarbons extracted primarily from the cycle oil. In general, the cycle oil extract will include about 40 to 90% (more narrowly, 70 to 80) phenol, and about 0 to 15% water, assuming that water is mixed with the phenol solvent during extraction. This cycle oil extract is employed to contact a heavy gas oil in extraction zone 27 which may be a tower, a tank mixer-settler combination, or a centrifugal extraction device. In the illustration, a tower is depicted.

In accordance with this invention, the cycle oil extract phase of line 26 is contacted with a virgin gas oil introduced to the system through line 10 for treatment in

tower 27. Preferably the cycle oil extract phase is used in amounts of about 125 to 225% based on the gas oil feed. The virgin gas oil of line 10 may constitute the gas oil fractions of a crude oil boiling above about 430° F. The present invention is of particular application to gas oils in the higher boiling range up to 1150° F., or somewhat higher in which higher concentrations of organic metal compounds exist. As indicated, such gas oils are characterized by inclusion of organic compounds containing metal contaminants such as nickel, vanadium and iron. These metallic compounds may be present in amounts of about 0.00002 to 0.001% or somewhat higher. The process of this invention is of application to such gas oils in permitting removal of the metal contaminants referred to.

In tower 27, contact of gas oil with the cycle oil extract phase results in the selective removal of metallic contaminants from the gas oil. Since the solvent present in the cycle oil extract is essentially saturated with high molecular weight, condensed ring aromatic hydrocarbons, extracted from cycle oil, substantially none of the gas oil is taken up by solvent in extraction tower 27. As a result, the raffinate product withdrawn from tower 27 through line 28 comprises the hydrocarbon composition of the heavy gas oil introduced to the tower through line 10, with the substantial exclusion of the metal contaminants originally present in the gas oil.

The extract phase removed from tower 27 through line 29 will constitute spent phenol solvent together with highly aromatic hydrocarbons extracted from cycle oil and metal contaminants removed from gas oil. Solvent may be recovered from this extract phase and the purified solvent can be recycled to line 14 constituting the phenol fed to tower 12. The concentrated aromatic hydrocarbons segregated in the extract phase are valuable for many purposes.

The raffinate products of line 25 and 28 are combined in line 30 and passed to distillation zone 31. Fractionation zone 31 is operated to permit removal of phenol through line 32 and to permit removal of hydrocarbon constituents of the combined raffinates through line 33. The phenol recovered through line 32 may be recycled to the system through line 14 of extraction tower 12. The hydrocarbon products of line 33 are then employed as the feed to catalytic cracking zone 1 supplied through line 2. In order to establish the novel and advantageous features of this invention, reference will be made to exemplary data showing the particular advantages of the multi-stage contacting described.

In order to demonstrate the operation of the first two stages of the process described, conducted in extraction zones 12 and 24, two phenol extraction units of a lubricating oil refining plant were converted to the processing principles of this invention. In one of the phenol extraction units, phenol was conventionally contacted with a lubricating oil distillate to produce a lubricant. Part of the lubricating oil extract phase was used as the solvent in the other of the phenol extraction units to contact cycle oil. A raffinate product adapted for use as catalytic cracking feed was produced from this second unit.

The lubricating oil distillate which was phenol extracted was produced from a blend of distillates obtained from Talco and North Louisiana crudes. A typical range of inspections follow for this stream:

Gravity, ° API	26.5-27.5
Viscosity, SSU/210° F.	39-42
Aniline point, ° F.	185-195
Diesel index	49-54

This distillate was treated with phenol in a countercurrent extraction tower providing about 5 theoretical stages. The feed rates were about 12,300 B./S. D. of phenol and about 7,450 B./S. D. of lube distillate to provide a phenol treat of 165%. Water injection was maintained during extraction to provide a total injection

amount of about 2.5%, based on the phenol. The extraction temperature was about 145° F.

The extract phase obtained from this operation, constituted 84% phenol; 2% water, and 14% hydrocarbons extracted from the lubricating oil feed. The hydrocarbon constituents of the extract phase were primarily mono-nuclear aromatic compounds having substantial alkyl side chain substitution. Phenol was separated from a portion of this extract phase and it was found that the hydrocarbon constituents of the extract phase had the following inspections:

Gravity, ° API	16.8
Viscosity, SSU/210° F.	48.5
Silica gel analysis:	
Aromatics, wt. percent	69.9
Paraffins, wt. percent	30.1
Conradson carbon, wt. percent	0.3
Aniline point, ° F.	130
Diesel index	22
Distillation, 10 mm. Engler:	
I. B. P., ° F.	366
5%	411
50%	490
90%	584

The economical disposition for these hydrocarbons is to catalytic cracking feed. Consequently, in normal oper-

ation expressed as the ratio of extract phase to cycle oil. About 5 vol. percent water, based on the extract phase, was injected during extraction. The temperature maintained during extraction was 130° F. at the top of the tower and 125° F. at the bottom of the tower. The raffinate from this operation was produced from both the cycle oil and the hydrocarbon extract in a yield of 73.2 vol. percent based on the cycle oil feed, or 62.9 vol. percent based on total oil feed. The raffinate product had the following inspections:

Gravity, ° API	30.3
Viscosity, SSU/210° F.	41.3
Silica gel analysis:	
Aromatics, wt. percent	25.8
Paraffins, wt. percent	74.2
Conradson carbon, wt. percent	0.11
Aniline point, ° F.	205.7
Diesel index	62.3
Distillation, 10 mm. Engler:	
I. B. P., ° F.	321
5%	390
50%	483
90%	576

For comparative purposes significant data including that of the foregoing tests are collected and reproduced as Table I below:

Table I

	Column 1	Column 2	Column 3	Column 4	Column 5	Column 6
	Cycle Oil Feed	Raffinate from Fresh Phenol Extraction of Cycle Oil at 90% treat, 6% H ₂ O	Hydrocarbon Extract from Lube Oil	Blend of Extract and Cycle Oil In Feed Prop.	Blend of Extract and Cycle Oil Raffinate In Prod. Prop.	Raffinate
° API	19.1	35.5	16.8	18.8	30.8	30.3
SSU/210° F.	41.8	39.1	48.5	42.6	40.6	41.3
Aromatics, Wt. percent	46.4	11.2	69.9	49.7	25.9	25.8
Paraffins, Wt. percent	53.6	88.8	30.1	50.3	74.1	74.2
Aniline Pt., ° F.	159	220	130			
Conradson Carbon content, Wt. percent	2.5		0.3			0.1
Diesel Index	30	78	22	29	66	62.3

ation, after removal of the phenol in phenol recovery facilities, extract is sent to catalytic cracking feed.

In accordance with one feature of this invention, the desirable portion of the hydrocarbon extract is recovered as raffinate from the extract phase when the extract phase is contacted with cycle oil. The quality of the hydrocarbon extract as catalytic cracking feed is accordingly improved. This operation was conducted in the second of the phenol extraction units employing a catalytic cycle oil having the following inspections:

Gravity, ° API	19.1
Viscosity, SSU/210° F.	41.8
Silica gel analysis:	
Aromatics, wt. percent	46.4
Paraffins, wt. percent	53.6
Conradson carbon, wt. percent	2.5
Aniline point, ° F.	159
Diesel index	30
Distillation, 10 mm. Engler:	
I. B. P., ° F.	212
5%	347
50%	479
90%	602
Initial atmospheric B. P., ° F.	430

This cycle oil was contacted with the lubricating oil extract phase in a countercurrent treating tower having about 5 theoretical contacting stages. A cycle oil feed of 6000 B./S. D. was maintained while introducing 7,020 B./S. D. of the extract phase equivalent to 117%

In this table, column 1 shows the inspections of the catalytic cycle oil used in these tests. Column 2 shows the nature of a raffinate product obtained by extracting this cycle oil with fresh, or in other words, pure phenol for comparative purposes with the process of this invention. Column 3 shows the inspections of the hydrocarbon portion of the lubricating oil extract phase referred to in the foregoing tests. Column 4 shows the inspections of a blend of the extract of column 3 and the cycle oil of column 1 in the proportions used as feed in the foregoing tests of this phase of this invention; 85.9% cycle oil and 14.1% extract. Column 5 shows a blend of the cycle oil raffinate of column 2 and the lubricating oil extract of column 3 in the proportions resulting from the tests exemplifying this phase of the invention; 77.1% raffinate and 22.9% extract. Finally, column 6 shows the inspections of the raffinate product resulting from the foregoing tests in accordance with the principles of this invention.

The inspections given above must be considered in connection with the initial characteristics of both the cycle oil feed to treating tower 17 (column 1) and the hydrocarbon extract feed to tower 17 (column 3). Thus, as mentioned above, the raffinate product shown in column 6 includes constituents from each of these streams so that in effect the raffinate product constitutes the segregated portion of both the cycle oil and the lube extract suitable for catalytic cracking feed. Comparing the inspections of the raffinate product to either those of the cycle oil feed or the hydrocarbon extract, it will

be observed that this product has substantially better characteristics for catalytic cracking feed than either the untreated cycle oil or the hydrocarbon extract. For example, it will be observed that the untreated cycle oil had a Conradson carbon content of 2.5 wt. percent and the hydrocarbon extract, 0.3 wt. percent, while the raffinate product from tower 17 had a Conradson carbon content of 0.1 wt. percent. Again the paraffin content of the raffinate product was raised to 74.2 wt. percent as against a value of 56.3 wt. percent for the untreated cycle oil and 30.1 wt. percent for the hydrocarbon extract. It is therefore shown that operation of the first two stages of the process illustrated in the drawing results in substantially upgrading a cycle oil and a hydrocarbon lube extract, serving to materially improve their value as catalytic cracking feed stocks.

By a similar comparison of the inspections of column 6 with the inspections of column 5, it is shown that the raffinate product of the extraction described is fully equivalent as a feed stock for catalytic cracking in comparison to a blend of lube oil extract and extracted cycle oil. This data, in combination with material balances, establishes that a raffinate product is obtained which segregates the hydrocarbon constituents of the extract phase from lubricating oil together with the less aromatic portion of cycle oil much as though these were separately prepared and blended. In other words, the volume of lubricating oil extract hydrocarbons present in spent phenol from a lubricating oil extraction process is directly added to the volume of cycle oil raffinate which would normally be obtained by the extraction of cycle oil with pure (or fresh) phenol at the same extraction conditions. Yet this is achieved without necessity for distilling phenol from the lubricating oil extract phase, avoiding the expensive solvent recovery facilities ordinarily required for this at this step of the process. Again, this is achieved without any loss in quality of the product as catalytic cracking feed.

These steps of the process illustrated in the drawing have additional features above and beyond those brought out heretofore. It is a particular feature that lubricating oil constituents, normally contaminated with metal compounds, are upgraded for catalytic cracking by substantial elimination of the metal contaminants. The metal contaminants referred to include compounds of nickel, vanadium, and iron which result in poisoning of the cracking catalyst so as to seriously decrease the selectivity and life of the catalyst. As indicative of the problem that exists, a typical lubricating oil fraction of a petroleum oil contained 0.58 p. p. m. of nickel. This lubricating oil was extracted with phenol at a temperature of about 215° F. using a 200% treat of phenol and 2% of water. Separation of solvent from the extract phase provided segregated hydrocarbon constituents suitable for catalytic cracking feed stock. However, extraction of lubricating oil ordinarily results in concentrating metal contaminants in the hydrocarbon extract so that in this case the extract contained 1.16 p. p. m. of nickel. Heretofore the use of lube extract for catalytic cracking has been severely debited because of this metal contamination.

In the practice of this invention, however, a catalytic cracking feed is obtained, including the hydrocarbons present in a lubricating oil extract phase, which is substantially free of metal contaminants. Referring to the drawing, for example, the lube extract present in line 16 is freed of metal contaminants in treating tower 24. Metal contaminants are removed from tower 24 through line 26 together with the extract phase of tower 24. The raffinate product of line 25, including the hydrocarbons originally present in the lube extract stream of line 16, is recovered for catalytic cracking free of metal contaminants. In a typical case 90% removal of nickel was obtained by this technique, providing a raffinate product

for catalytic cracking containing the extremely low nickel content of 0.02 p. p. m.

The data presented heretofore has concerned the preparation of a cycle oil extract phase as obtained in treating tower 24 illustrated in the drawing. It has been shown that extract and raffinate phases of cycle oil, useful in the process of this invention, can be obtained by treating cycle oil with a selective solvent by itself. It has also been shown that particular advantages are secured if this is achieved by treating cycle oil with the total extract phase of a lubricating oil extraction process. As pointed out, in either case a cycle oil extract phase is obtained constituting a major portion of spent solvent and a minor portion of aromatic hydrocarbons extracted from the cycle oil. It is a particular feature of this invention that the total cycle oil extract phase be employed as an extraction agent for the treatment of a virgin gas oil as conducted in tower 27 of the drawing.

In order to demonstrate the portion of the process conducted in tower 27, experiments were conducted in which a cycle stock extract phase derived by contact of cycle oil with lube oil extract phase as indicated in the foregoing experimental results was contacted with a heavy gas oil. The cycle stock extract phase constituted 70% phenol and 30% oil. The hydrocarbon portion of this extract phase had the following inspections:

Gravity, °API	1.8
Viscosity, SSU/210° F.	51.8
Silica gel analysis:	
Aromatics, wt. percent	84.6
Paraffins, wt. percent	15.4
Conradson carbon, wt. percent	6.5
Distillation, 10 mm. Engler:	
I. B. P.	253
5%	340
50%	466
90%	620
Aniline point, °F	109
Diesel index	2

This cycle oil extract phase was employed to contact a gas oil having the following inspections:

Gravity, °API	21.2
Viscosity, SSU/210° F.	116
Conradson carbon, wt. percent	2.29
Sulfur, wt. percent	0.39
Nickel, p. p. m.	2.1
Percent aromatics, wt. percent	39.9
Percent paraffins, wt. percent	60.1

The cycle oil extract phase and gas oil were contacted in an extraction unit providing about 5 stages of theoretical contacting. The extraction was carried out at a temperature of about 160° F. providing a phenol treat of 114 volume percent based on the cycle stock extract phase. The hydrocarbons present in the raffinate resulting from this contact had the following inspections:

	Volume percent
Yield of cracking feed	113
Gravity, °API	18.5
Viscosity, SSU/210° F.	77.5
Conradson carbon, wt. percent	1.60
Nickel, p. p. m.	0.3
Percent aromatics, wt. percent	45.5
Percent paraffins, wt. percent	54.5

It will be noted from this data that contact of the gas oil with the cycle stock extract resulted in substantial elimination of metal contaminants from the gas oil (87.0% removal) while permitting substantially complete recovery of all constituents of the gas oil suitable for use as catalytic cracking feed. In fact, as indicated by the 113% yield based on gas oil feed, the process was operative to recover the more paraffinic type hydrocarbons originally present in the cycle oil extract phase. This is

borne out by the fact that the cycle oil extract phase used to contact the gas oil had an aromatic content of 84.6% while the resulting extract phase had an aromatic content of about 94.5%.

A critical feature of this invention is the use of separate contacting stages for the extraction of cycle stock and gas oil. In order to show the benefits of staged contact, reference is made to the following exemplary data:

In a first series of experiments, cycle stock and gas oil were mixed together and contacted with a lubricating oil extract phase in a single stage contacting operation. In a second, comparative series of experiments, the same catalytic cycle stock and the same gas oil were separately extracted in a two-stage operation. In this case, the cycle oil was first contacted with the lubricating oil extract phase to form a cycle oil extract phase. This cycle oil extract phase was then contacted with the gas oil in a second stage contacting operation. These experiments established that substantially better extraction results could be obtained by the two stage contacting as compared to the single stage contacting. The unique advantage of plural stage contacting resides in the recovery of greater yields of raffinate product suitable for cracking while securing equivalent or superior removal of metal contaminants. To clearly show this, the tabulated data following was chosen for comparative single and double stage contacting adjusted to secure the same amount of raffinate product. It will be noted that substantially better nickel removal was obtained in the two stage process.

Extraction Process Conditions	Single Stage	Two-Stage
Phenol Treat, Vol. Percent.....	90-100	90-100
Extraction Temperature, °F.....	160	160
Feed Composition, Vol. Percent:		
Catalytic Cycle Stock.....	50	50
Contaminated Gas Oil.....	50	50
Total Yield of Raffinate on Total Oil Feed, Vol. Percent.....	78.7	78.7
Nickel Removed from Oil, Percent of Input.....	78	95

This data brings out the substantial advantages obtained from the staged extraction process of this invention. The data shows that by employing two contacting stages as described in place of a single contacting stage, substantially better removal of nickel contaminants from gas oil is secured.

Additional benefits also exist for this two stage process. In order to appreciate their significance, reference may be made to a typical plant situation. Assuming the availability of lube oil spent solvent to be 20,000 B./D. with a solvent content of 85 vol. percent, it can be seen that a maximum of 19,666 B./D. of combined cycle stocks-gas oils can be extracted in a single stage operation at a 75% solvent treat (defined as volume of solvent per volume of total oil). In a two stage process, a maximum of 29,799 B./D. of cycle stocks-gas oils can be extracted at the same 75% solvent treat. In this example, maximum permissible feed rate at constant treat is increased by about 10,133 B./D. or 51%.

As described, this invention concerns extraction operations in which virgin and cracked gas oil fractions of a petroleum oil are separately extracted with a selective solvent for aromatic hydrocarbons wherein the total extract phase resulting from one extraction step is used in the second extraction step. Two of the most important applications of this invention have been brought out in the foregoing description and data. In one of these, fresh selective solvent is employed to extract cycle oil and the extract phase from this extraction step is then used to extract virgin gas oil. As established, the aromatic constituents of the gas oil present in the cycle oil extract phase serve to improve removal of metal contaminants from the gas oil. The full advantages of this technique are also achieved in the preferred embodiment

of the invention illustrated. In this case, fresh solvent is first used to extract the lubricating oil fraction of a virgin gas oil. The extract phase from this operation is then employed to extract cycle oil. Finally, the cycle oil extract phase is used to extract gas oil. It is apparent that the advantages of this invention can be achieved to a lesser extent by use of additional contacting stages with the total extract phase of each stage being used as the extraction agent in successive stages. For example, in the case just described, the gas oil extract phase could be used in a subsequent extraction of virgin gas oil in order to secure greater removal of metal contaminants than obtainable by use of fresh solvent.

The principles governing these and other permutations of the treating stages described can be appreciated by comparative data showing the general magnitude of metal removal possible from a gas oil for different extraction agents at comparable conditions: about 77% of the nickel contaminants present in a virgin gas oil can be removed by extraction with fresh phenol; about 86% of the nickel can be removed by extraction with the extract phase of a lubricating oil extraction step; and about 95% of the nickel can be removed by using cycle oil extract phase. While this data establishes that the embodiment of the invention described is best adapted for metal removal, it must be recalled that the invention is also of utility for minimizing aromaticity of catalytic cracking feed stock.

Thus, for example, it is within the scope of this invention to employ fresh solvent to extract lubricating oil, using the lube extract phase to extract virgin gas oil, and using the gas oil extract phase to extract cycle oil. Removal of metal contaminants from the gas oil in this sequence of steps is somewhat inferior but the combination process does serve to provide the objective of minimizing the aromatic hydrocarbons in cracking feed. Again, if desired, fresh solvent can be used to extract gas oil with the gas oil extract phase being used to extract cycle oil in order to recover gas oil extract constituents suitable for cracking.

Among these variations of the invention, a preferred process entails use of the solvent extract phase from a lubricating oil extraction process to extract gas oil at treats of about 100-250% providing a first raffinate product and an aromatic extract phase. This aromatic extract phase is then used to extract cycle oil at treats of about 50-300% to provide a second raffinate product. The combined raffinate products are of high quality for catalytic cracking feed. Tests which have been carried out show that this sequence of treating steps serves to provide an over-all removal of nickel contaminants of about 60-75% based on gas oil input. In this treating combination, it is particularly contemplated to use a portion of the lubricating oil extract phase as a wash for cycle oil raffinate, thereby further reducing the metal content of this stream. Volumetrically, the paraffinic part of catalytic cycle stock and essentially all of the recycle gas oil are recovered as catalytic cracking feed.

What is claimed is:

1. An improved extraction process for the preparation of catalytic cracking feed stocks including in combination the steps of: contacting a lubricating oil distillate with a selective solvent for aromatic hydrocarbons, segregating a lubricating oil extract phase, contacting a catalytic cycle oil with said lubricating oil extract phase, segregating a cycle oil extract phase, contacting a virgin gas oil including constituents boiling up to at least about 1100° F. and containing metallic contaminants with said cycle oil extract phase, and segregating a gas oil raffinate phase substantially free of metallic contaminants.

2. A combination catalytic cracking and extraction process in which catalytically cracked products boiling above about 430° F. are segregated and contacted with a selective solvent for aromatic hydrocarbons forming extract and raffinate phases, recycling hydrocarbons in

13

said raffinate phase to catalytic cracking and contacting a virgin gas oil fraction including constituents boiling up to at least about 1100° F. and containing metallic contaminants with said extract phase, forming a gas oil extract phase and a gas oil raffinate phase substantially free of metallic contaminants, and passing hydrocarbons in said gas oil raffinate phase to catalytic cracking.

3. In the extraction of metal contaminants from a gas oil fraction including constituents boiling up to at least about 1100° F. by contact with a selective solvent for aromatic hydrocarbons, the improvement which comprises contacting said gas oil fraction with spent selective solvent constituting the extract phase resulting from prior contact of the said selective solvent with hydrocarbons boiling above 430° F. selected from the group consisting of lubricating oil distillates and cycle oil, and recovering a gas oil raffinate phase substantially free of metallic contaminants.

4. A method of extracting the metal contaminants from a straight run heavy gas oil fraction including constituents boiling up to at least about 1100° F. which comprises in combination contacting a lubricating oil fraction with a selective solvent for aromatic hydrocarbons to form lube oil raffinate and extract phases, segregating the lube oil extract phase and contacting the same with a cycle oil to form cycle oil raffinate and extract phases, segregating the cycle oil extract phase and contacting the same with said straight run heavy gas oil to form separate gas oil raffinate and extract phases, said gas oil raffinate phase being substantially free of metallic contaminants and said gas oil extract phase containing metal contaminants from the heavy gas oil.

5. A combination catalytic cracking and extraction

14

process wherein a straight run heavy gas oil including constituents boiling up to at least about 1100° F. and containing metallic contaminants is employed as the catalytic cracking feed stock which comprises in combination the steps of contacting a lube oil fraction boiling above about 500° F. with a selective solvent for aromatic hydrocarbons to form lube oil extract and raffinate phases, segregating the lube oil extract phase and contacting the same with a cycle oil boiling above 430° F. from a catalytic cracking operation to form separate cycle oil raffinate and extract phases, contacting the cycle oil extract phase with said straight run heavy gas oil to form separate gas oil raffinate and extract phases, said gas oil raffinate phase being substantially free of metallic contaminants and said gas oil extract phase containing metallic contaminants from said straight run gas oil, segregating the gas oil component of the gas oil raffinate phase and subjecting said component to catalytic cracking.

6. A process as defined in claim 5 in which the cycle oil component of the cycle oil raffinate phase is segregated from raffinate phase and is catalytically cracked.

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