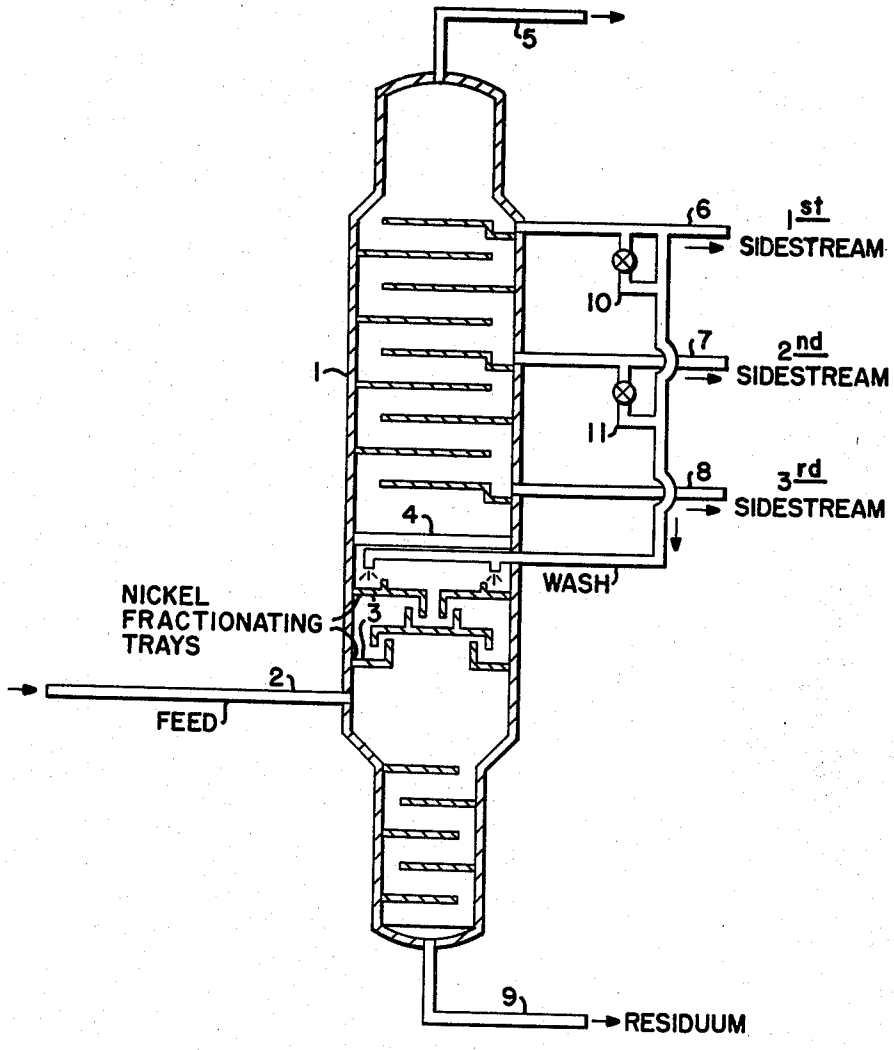
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PREPARATION OF CATALYTIC CRACKING FEED STOCKS

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PREPARATION OF CATALYTIC CRACKING FEED STOCKS

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The present invention concerns a novel distillation process operative to reduce the content of metal contaminants present in catalytic cracking charge stocks. The invention more specifically relates to an improvement in the distillation of metal containing crude oil whereby the yield of catalytic cracking feed stock is increased and that of residuum and high boiling residual oil is decreased. Still more specifically, the present invention relates to an improved refluxing agent in such a distillation operation.

In recent times, a great deal of effort has been applied in the petroleum refining field to increase the recovery of catalytic cracking feed stock from residual fractions of petroleum oil. Conventionally, the feed stock to a catalytic cracking operation constitutes a so-called gas oil fraction of crude oil which boils in the range of about 400° to 800° F. or somewhat higher. Portions of the petroleum crude oil boiling above the gas oil boiling range may be considered residual petroleum fractions. Such residual fractions may be used as sources of asphalt, fuel and other products which are of relatively low economic value. It, therefore, becomes attractive to develop means for successfully utilizing portions of the residual fractions of crude oil as catalytic cracking feed stock.

Attempts to employ heavier fractions of crude oil for catalytic cracking have been limited heretofore due to the presence of certain metal contaminants in such heavy fractions. Thus the highest boiling fractions of a crude oil contain substantial portions of metal contaminants, particularly including nickel, vanadium and iron compounds. The residual fractions of typical crude oils generally contain these metal contaminants in quantities of about 10 to 500 pounds per 1000 barrels of residual fraction. When an attempt is made to segregate higher boiling distillate fractions of a crude oil, some portion of these metal contaminants are inherently and unavoidably carried over into the distillate products. For example, in a vacuum distillation operation where a heavy boiling gas oil fraction is segregated from a crude oil, about 0.5 to 10 pounds per 1000 barrels of metal contaminants will be obtained in the gas oil distillate in a typical situation. In this example, the gas oil distillate referred to would have a boiling range of about 700° to 1100° F.

The problem of metal contaminant carry-over in the segregation of heavy distillate fractions is apparently due to two phenomena. First of all, it appears that the metal contaminants occur or are converted during distillation to the form of metal complexes. These complexes may generally be identified as large condensed ring substances. Some of these metal complexes and particularly nickel porphyrins are sufficiently volatile so as to be carried overhead at a temperature of about 1050° F. Consequently, when attempting to segregate heavy boiling gas oil fractions including components boiling above about 900° F., volatile metal contaminants are unavoidably obtained in the distillate product. It appears that a second phenomena is also involved which may be referred to as

mechanical entrainment. To indicate generally the mechanism of this effect, it can be considered that a small portion of high boiling liquid hydrocarbons from the residual fraction is normally entrained overhead in a distillation operation. Since such liquid hydrocarbons contain concentrated amounts of metal contaminants, such entrainment in distillate products accounts for a portion of the metal contamination of such distillates.

By virtue of the fact that catalytic cracking operations are adversely affected by the presence of such metal contaminants, it is apparent that the need exists for some means to recover high boiling fractions of a crude oil while eliminating contamination in the manner described. The presence of metal contaminants and particularly nickel in a catalytic cracking operation results in direct contamination of the catalyst by the metal compound. Metal continues to accumulate on the catalyst during the life of the catalyst having the result of seriously altering the catalytic properties of the catalyst. In general, it is considered essential to reduce the metal contaminant content of the catalytic cracking feed stock to a value of less than about 3 pounds per 1000 barrels. It is the principal object of this invention to provide this objective in a novel and practically attractive manner.

Petroleum crude oil is normally distilled in a vacuum tower operated at pressures of about 25 to 250 mm. mercury; initially, it may be given a preliminary fractionation in an atmospheric distillation tower to provide a bottoms fraction constituting a reduced crude oil boiling above about 600° F. The reduced crude oil undergoes a flashing operation so that light portions of the reduced crude are carried overhead in vapor form and the heaviest boiling fractions are carried downwardly toward the bottom of the tower. As pointed out, entrainment of metal contaminants and also of residuum into the overhead vapors is a serious problem. To avoid this, entrainment screens and bubble cap or other type trays are incorporated into the towers, and a portion of the bottoms sidestream is conventionally pumped back as reflux to the bubble cap trays.

Normally a portion of the heavy gas oil bottoms sidestream is pumped to the nickel fractionating trays below the entrainment screen as a wash oil reflux. The volume of wash oil is usually about 10 to 20% of the reduced crude. The heavy gas oil is refluxed at approximately its bubble point, about 700° F. The heavy gas oil is an oil having approximately a 550° F. @ 10 mm. of Hg and heavier boiling range cut. This heavy gas oil may have a viscosity of 90 to 150 SSU @ 210.

An important problem in connection with the use of this bottoms sidestream as a wash solvent is the gradual deterioration of the entrainment screen. These screens, of which there may be one or more in the still, tend to coke up rapidly and thus become ineffective in removing entrainment. The effective entrainment screen life has been found to be a function of the temperature to which it is subjected.

There is, of course, a large incentive to reduce residuum yields at the vacuum pipe stills and thereby upgrade residuum to the more valuable cracking feed stock. One way of doing this is to increase the vacuum furnace coil outlet temperature, but this increases the screen temperature and thus reduces the screen life and service factor of the unit. Clean screens are very effective in removing entrainment, but as the run length progresses the screen gradually cokes up causing a reduction in entrainment removal efficiency. The effective life of an entrainment screen is a function of the screen temperature, and screen temperature in turn is a function of the furnace coil outlet temperature. Therefore, lowering the residuum yields by raising the furnace coil outlet temperature results in a higher screen temperature and thus a shorter

screen life. The screen temperature is especially critical if the temperatures are in the 750° to 800° F. range since about an 18° F. increase in screen temperature will halve the screen life in this range. Operation with a fouled screen is uneconomical because considerable debits for entrained residuum and metals are incurred when the screen efficiency drops.

The bottoms sidestream wash has been found to be a major contributor to the high residuum yields. Thus, any portion of this extractive distillation stream that does not vaporize when passed over the fractionating tray passes downward into the residuum and thus increases residuum yields.

The present invention is based on the discovery that by introducing a substantially lighter wash stream into the distillation tower, not only can metals be removed from the distillate fractions by the principles of extractive distillation, but also substantial decrease in residual oil formation is realized. Substantially more of the oil is vaporized on the fractionating trays, and less spills over into the lower part of the tower to form residuum. Furthermore, with the increased vaporization there is realized a substantially greater cooling effect on the vapor coming from the flash zone, and thereby the temperature of the screen is lowered. This enables the coil outlet temperature to be raised to maintain a constant screen temperature at a level whereby coking is minimized and screen life extended substantially. With the raising of the coil outlet temperature the residuum yield is even further reduced.

A lighter wash may be taken from any pump around or sidestream above the bottoms sidestream. However, care must be taken not to use a wash light enough to flash upon entering the tower and leave the nickel fractionating tray dry. A wash in the 350° to 700° F. @ 10 mm. boiling range is considered practical. The volume of light wash is normally 10 to 20% of the reduced crude. Preferred is a light gas oil fraction boiling in the range of about 700° to 900° F. at atmospheric pressure; viscosity about 50 to 80 SSU @ 210.

Particularly useful as entrainment screens are those made of wire mesh. One or more may be positioned in the fractionation area of the tower.

In the practice of this invention, the light wash oil described above is injected into the distillation zone in proportions of about 10 to 20% based on the hydrocarbon vapor rate at the portion of the distillation zone at which the refluxing agent is injected. The lower limit of the amount of refluxing agent to be used is determined by the concentration of metal contaminants in the stock distilled coupled with the amount of cooling desired at the screens. It is essential that the refluxing agent be brought into the distillation tower at a point below the screen and above the uppermost of the fractionating trays, which point is above the feed inlet. The wash oil must be brought into intimate contact with the upflowing hydrocarbon vapors in the tower, and thus is deposited over at least one plate in the distillation tower.

Referring now to the accompanying drawing showing a preferred embodiment of the present invention, numeral 1 identifies a distillation tower for segregation of the fractions of a petroleum crude oil. Tower 1 can particularly constitute a vacuum still operated at pressures of about 25 mm. to 250 mm. Hg. Reduced crude is brought into tower 1 through line 2 at temperatures of about 700° to 860° F. The reduced crude oil undergoes a flashing operation in the lower portion of vacuum distillation tower so that light portions of the reduced crude including the gas oil fractions are carried overhead in vapor form, and the heaviest boiling portions are carried downwardly towards the bottom of the tower.

Above the feed inlet line 2 are positioned one or more fractionating trays 3, which serve to reflux the ascending vapors and the wash solvent. Above the trays there is disposed screen 4, which serves principally to remove entrained residuum.

The lightest boiling fractions are withdrawn through line 5, while successively higher boiling fractions are removed from sidestream withdrawals 6, 7 and 8. Ordinarily, the heaviest fractions of the reduced crude are subjected to a steam stripping operation in the bottom of the distillation tower, and the stripped products constituting residual crude oil are then withdrawn through bottoms withdrawal 9.

To provide the reflux wash of the present invention, a stream of light wash withdrawn from lines 6 and/or 7 through lines 10 and/or 11 is continuously passed into still 1. The composition of this stream and its boiling range have previously been specified, and in general it is preferred to employ amounts of refluxing agent in the range of about 10 to 20% based on the hydrocarbon vapor rate. By means of this recycle, the coil outlet temperature of the feed may be raised to about 830° F., resulting in substantial decrease in residue formation, without causing excessive coking of screen 4.

The process of the present invention may be further illustrated by the following specific examples:

The following table shows the effect of changing to light wash at one of the vacuum pipe stills:

TABLE I

Wash	Coil Outlet Temp., ° F.	Screen Temp., ° F.	Vol. Wash Percent Reduced Crude	Residuum Yield Percent on Crude
Heavy	825	760	20	5.00
Light	825	757	20	4.55
Light	828	760	20	4.37

In addition to the advantage pointed out in the above table, the light wash also has less tendency to crack. This is important since the nickel fractionating trays are often badly fouled during the run length due to coke formation as a product of cracking.

The decrease in residuum formation of 0.6% is a highly desirable result from an economic point of view. Thus in a single unit processing 80,000 barrels per day, this represents an increase in yield of gas oil of 480 barrels a day, or 150,000 barrels a year.

The importance of the screen temperature on the life thereof is shown in Table II:

TABLE II

Effect of screen temperature on screen life

Screen Temperature, °F.:	Screen Life, Mo.
750	8.0
760	6.0
770	4.5
780	3.5
790	2.0

What is claimed is:

1. In a distillation process wherein a metals contaminated petroleum hydrocarbon feed stock containing a substantial portion of hydrocarbon constituents boiling above 900° F. is charged to a distillation zone and fractionated therein to segregate a gas oil fraction, the improvement which comprises maintaining a fractionation zone within said distillation zone, further maintaining a metallic screening zone superimposed above said fractionation zone and adapted to screen out entrained contaminants, and passing a wash oil boiling in the range of from about 700° to 900° F. into said zone at a point intermediate said fractionation and said screening zones.

2. The process of claim 1 wherein said wash oil is a portion of said gas oil fraction.

3. The process of claim 1 wherein said first named hydrocarbon fraction is a reduced crude.

4. The process of claim 3 wherein 10 to 20% of said

wash oil, based on reduced crude, is recycled to said distillation zone.

5. In a distillation process wherein a metals contaminated petroleum hydrocarbon feed stock containing a substantial portion of hydrocarbon constituents boiling above 900° F. is charged to a distillation zone and fractionated therein to segregate gas oil fraction, the improvement which comprises maintaining a fractionation zone within said distillation zone, further maintaining a metallic screening zone at a temperature of from about 750–800° F. superimposed above said fractionation zone and adapted to screen out entrained contaminants, and passing a wash oil boiling in the range of from about 700–900° F. into said zone at a point intermediate said fractionation and said screening zones.

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