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PRETREATMENT OF CATALYTIC CRACKING FEED TO REMOVE METALS

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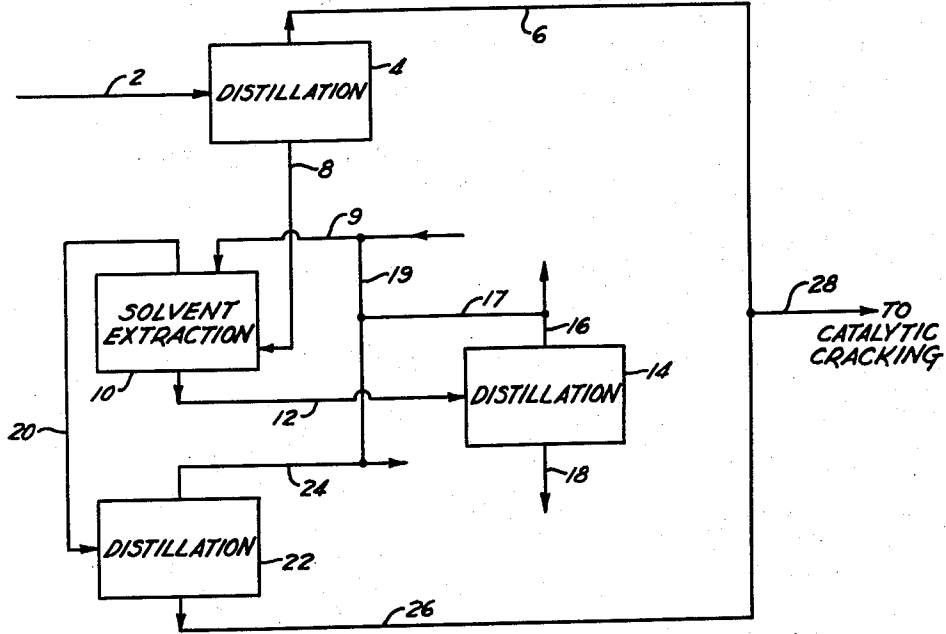


Fig. 1

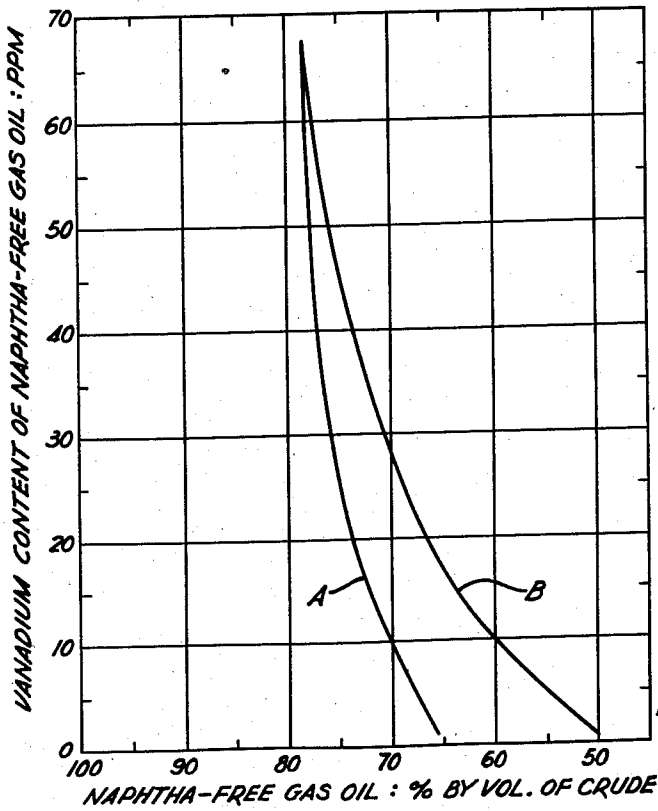


Fig. 2

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**PRETREATMENT OF CATALYTIC CRACKING
FEED TO REMOVE METALS****Robert E. Donaldson, Penn Township, Allegheny County,
Pa., assignor to Gulf Research & Development Com-
pany, Pittsburgh, Pa., a corporation of Delaware****Application May 18, 1956, Serial No. 585,793****6 Claims. (Cl. 208—87)**

This invention relates to improved procedure for catalytic cracking of charge stocks which contain metalliferous impurities.

Large quantities of metalliferous containing crudes, fractions thereof and hydrocarbons derived therefrom contain harmful amounts of metalliferous impurities, especially vanadium compounds. These metalliferous impurities are frequently present in such large amounts that utilization of the petroleum or fraction thereof is a real problem. Thus catalytic cracking of such crudes or fractions of such crudes is either expensive or uneconomical because the metalliferous impurities harmfully affect selectivity of the catalyst. For this reason, such crudes, fractions or products derived therefrom have not been utilized to the fullest possible extent.

This invention has for its object to provide improved procedure for catalytic cracking of fractions of crude petroleum or hydrocarbons derived therefrom which contain metalliferous impurities in sufficient amount to harmfully affect selectivity of a cracking catalyst. Another object is to provide an improved combination of solvent extraction of such metalliferous containing oils followed by catalytic cracking. Another object is to provide procedure whereby the foregoing difficulties can be overcome or minimized. Other objects will appear hereinafter.

These and other objects of my invention are accomplished by subjecting a catalytic cracking charge stock which contains metalliferous impurities to distillation to separate a lower boiling fraction containing a smaller amount of metalliferous impurities than the original charge stock and a higher boiling fraction containing a larger amount of metalliferous impurities than the charge stock, extracting the higher boiling fraction with a solvent having selectivity for aromatic hydrocarbons and subjecting the extracted high boiling fraction (i.e. the raffinate) to catalytic cracking.

In the following examples and description I have set forth several of the preferred embodiments of my invention, but it is to be understood that they are given by way of illustration only and not in limitation thereof.

I have found that solvents which have a preferential solvent power or selectivity for aromatic hydrocarbons contained in hydrocarbon oil mixtures can be used to extract the metalliferous impurities. I prefer to utilize furfural, acetonitrile, dimethyl formamide, dimethyl sulfide or mixtures thereof to extract the higher boiling fraction.

My invention is applicable to any charge stock for catalytic cracking which contains metalliferous impurities in sufficient amounts to harmfully affect selectivity of a cracking catalyst. My invention is of particular value in connection with charge stocks which contain vanadium and/or nickel. I have found that the metalliferous impurities are present as organic-metallo compounds and that they can be preferentially removed from the higher boiling fraction of the charge stock by extraction with solvents having a selectivity for aromatic

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hydrocarbons. The distillation removes a lower boiling fraction which contains a smaller amount of the metalliferous impurities than the original charge stock so that concentration of the metalliferous impurities in the residue or higher boiling portion takes place and their removal by the solvent extraction is made more efficient. My invention is particularly applicable to the treatment of light or heavy gas oils having a boiling range normally charged to catalytic cracking operations. All charge stocks to catalytic cracking operations contain components having different boiling points. Therefore it is entirely feasible to separate a lower boiling and a higher boiling fraction from all such charge stocks. However, my invention is preferably applied to gas oils having a relatively wide or full range boiling point. Most gas oils conventionally charged to catalytic cracking have such a wide boiling range. The charge stock may be a straight run or virgin charge stock, or it may be derived from operations such as visbreaking, fluid coking or continuous contact coking, etc. Charge stocks containing not more than about 1.5 parts per million of vanadium or 0.6 part per million of nickel but preferably less than about 0.5 part per million of vanadium or 0.2 part per million of nickel (which are present as organo compounds as explained above) are generally desirable for catalytic cracking, i.e. metalliferous contents above these ranges have a harmful effect on the cracking catalyst. It will be apparent that oils having metal contents in these ranges are not the only oils which may be treated. For instance, a mixture of vanadium and nickel may be as harmful as a single metal even though the individual amounts of each metal are below the values mentioned above, i.e. the effect of the total amount of the metalliferous components would be sufficient to give harmful effects during catalytic cracking. My invention is also applicable to the treatment of catalytic cracking charge stocks containing any other metal which has a harmful effect on the selectivity of a cracking catalyst.

The initial distillation should be carried out to separate a low boiling fraction representing a substantial portion of the charge stock. The amount separated as the low boiling fraction will depend upon the boiling range or boiling points of the components of the charge stock. Furthermore it will depend upon the nature of the metalliferous compounds present. As a practical matter the low boiling fraction should be one which is relatively free of metalliferous impurities. In the case of vanadium or nickel impurities it should not exceed about one part per million metal content and preferably should be less than about 0.5 part per million in metal content. Usually removal of about 50 to 90 percent of the charge stock as light fraction will result in metal content within the range mentioned. However, larger or smaller amounts of removal may be used to obtain the desired low boiling fraction. The initial distillation may be carried out using any distillation procedure to separate components of the charge stock having different boiling points. Atmospheric, vacuum, steam, etc. distillation may be used for this purpose.

The solvent extraction may be carried out in a batch operation, i.e. the higher boiling fraction may be thoroughly mixed with the solvent and the two components permitted to stratify into separate layers with decanting of one of the layers. However, I prefer to employ countercurrent solvent extraction. When operating with furfural and using countercurrent extraction, the furfural would be introduced into the top of the extractor and the high boiling hydrocarbon oil fraction into the bottom of the extractor. The two components flow through the extractor countercurrently and the raffinate is removed from the top and the furfural and extract

from the bottom. The extract is then distilled to separate the solvent from the extract and the solvent then may be re-used. The temperature of extraction should not be so low as to be below the pour point of the hydrocarbon nor so high as to cause undue miscibility of hydrocarbon and solvent. In general the temperature may be between about -10° F. and about 250° F. and preferably between about 10° F. and about 200° F. The use of a temperature as low as possible is desirable since it enables the use of smaller amounts of solvent. The amount of furfural employed will generally be between about 0.25 and about 10 and preferably between about 1 and about 5 parts of furfural to oil. In the case of acetonitrile, the generally useful and preferred ranges are between about 1 and about 20 and about 3 to about 10. For dimethyl formamide they are 0.25 to 7 and 0.5 and 3. Dimethyl sulfoxide containing 0 to 10 percent water will generally be used in amounts of about 0.5 and about 10 and preferably between about 1.5 and 5 parts to 1 part of hydrocarbon oil. The larger amounts or proportions of solvents mentioned should be used when more complete removal of the metals is desired.

The raffinate from the solvent extraction process is preferably distilled to remove the residual or occluded solvent. This may be accomplished by simple distillation, fractionation or by stripping with gas, etc. The heavy fraction is then subjected to catalytic cracking, preferably after combining with the low boiling fraction from the initial distillation or with any other hydrocarbon which is a suitable cracking stock. The catalytic cracking operation may be carried out in any conventional manner. Thus it may utilize a fluidized cracking catalyst, a fixed bed of cracking catalyst or a moving bed cracking catalyst in which the catalyst is caused to flow through the reactor in the form of pellets.

In Figure 1 of the accompanying drawing I have illustrated diagrammatically a preferred modification of my invention. Referring to the drawing, numeral 2 indicates a conduit for introducing catalytic cracking charge stock into still 4 where a lower boiling fraction is removed overhead through conduit 6 and a higher boiling fraction removed as bottoms through conduit 8. The bottom fraction flows into continuous countercurrent solvent extractor 10 where it is extracted with furfural introduced through conduit 9, and the extract plus furfural is removed through conduit 12 and subjected to distillation in still 14. Furfural is taken overhead through conduit 16 and may be re-used by returning to extractor 10 through conduits 17, 19 and 9. The extract is removed through conduit 18 and may be used for any desired purpose such as a fuel. The raffinate or high boiling fraction is removed from extractor 10 through conduit 20 and is subjected to distillation in still 22 to remove occluded furfural which is taken overhead through conduit 24. This overhead furfural may be re-used by returning to extractor 10 through conduits 19 and 9. The solvent-free raffinate is removed through conduit 26 and is combined in conduit 28 with the lower boiling fraction which flows from still 4 through conduit 6. The combined mixture is then subjected to catalytic cracking.

EXAMPLE

A naphtha-free catalytic cracking charge stock prepared by vacuum reduction of mixed Western Venezuela tar oil (representing 4.6%–82.8% of the crude on fractional distillation) was subjected to equilibrium flash vaporization and the lower boiling portion (representing 4.6%–54.3% on the crude) was separated as distillate. The bottoms product from this distillation representing 54.3%–82.8% on the crude was batch extracted with furfural using a solvent to oil ratio of 2.24 and a temperature of about 140° F. The mixture was allowed to settle and the upper hydrocarbon layer separated by decantation. The lower furfural layer was distilled under vacuum to remove the furfural. The raffinate layer was

likewise subjected to vacuum distillation to remove furfural. The characteristics of the initial catalytic cracking charge stock representing 4.6%–82.8% on the crude is given in column 1 of Table I, the characteristics of the high boiling fraction prior to extraction are given in column 2 of Table I, the characteristics of the raffinate are given in column 3 of Table I and the characteristics of the extract are given in column 4 of Table I.

Table I

	Column 1	Column 2	Column 3	Column 4
Operating conditions:				
Temperature, $^{\circ}$ F.			130-145	
Solvent-to-Oil ratio, vol./vol.			2.24	
Yields: (Corrected to 100% weight balance—furfural free.) ¹				
Raffinate, percent by weight of charge.			77.1	
Extract, percent by weight of charge.			22.9	
Raffinate, percent by vol. of charge.			79.0	
Extract, percent by vol. of charge.			21.0	
Raffinate, percent by vol. of crude.			22.5	
Extract, percent by vol. of crude.			6.0	
	4.6-82.8% charge	54.3-82.8% charge	Raffinate	Extract
Inspections:				
Characterization factor	11.58	11.43	11.59	10.76
Gravity, $^{\circ}$ API.	17.6	10.8	13.9	-1.1
Viscosity, SUS, sec. at—				
130 $^{\circ}$ F.	386	28,460	10,355	82,326
210 $^{\circ}$ F.	71.3	944	549	1,485
Flash, P-M, $^{\circ}$ F., ASTM D93-46	295	570	395	
Pour point, $^{\circ}$ F., ASTM D97-47	-10	+65	+45	
Sulfur, Braun-Shell, percent	2.56	3.00	2.64	
Carbon residue, Conradson, percent, ASTM D189-46	3.66	10.3	6.05	8.0
Furfural, percent			0.13	
Aniline point, $^{\circ}$ F., ASTM D611-51T	150	161	181	
Bromine number, ASTM D1158-51T	19.1	24.6	24.0	
Distillation, vacuum corrected to 760 mm. Hg:				
Over point, $^{\circ}$ F.	379	585	628	
10% at $^{\circ}$ F.	565	976	922	
30% "	713		1,000	
50% "	840			
70% "	970			
90% "	>1,000			
Ash, Humble, p.p.m.		382	211	1,450
Metals, p.p.m.:				
Vanadium	67.5	174.5	57.1	665
Nickel	6.5	18.4	8.5	55.3

¹ Volume yields calculated from percent by weight yields and specific gravity of products and then corrected to 100% volume balance.

It will be noted that the vanadium content of the heavy fraction was reduced by the procedure of my invention from 174.5 to 57.1 parts per million with a volume decrease of 21.0 volume percent based on the heavy fraction.

Table II presents data comparing the method of my invention with conventional vacuum distillation for the preparation of a catalytic charge stock of a given vanadium content from the same 4.6%–82.8% fraction discussed in Example I. Table II, column 1 shows the results obtained by vacuum distillation to lower the metals content and prepare an improved catalytic cracking charge stock. Column 2 shows the results obtained by the process of the present invention on the same starting material and procedure described in Example I. It will be noted from comparing columns 1 and 2 that a 7.6 volume percent on the crude yield improvement may be realized by employing the procedure of the present invention. On the basis of these data I have calculated the possible improvement in yield if a catalytic charge stock of 1 part per million vanadium content were prepared from the

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same charge stock utilizing vacuum distillation as compared with the procedure of my invention. Column 3 of Table II gives the results of these calculations on the basis of utilizing vacuum distillation to prepare the catalytic cracking charge stock while column 4 shows the results of these calculations if the procedure of the present invention were employed. The procedure of the present invention gives a yield increase of about 15.8 volume percent on the crude over conventional vacuum distillation procedure.

Table II

	Col. 1	Col. 2	Col. 3	Col. 4
Yield of naphtha-free catalytic charge stock, percent by volume on crude.	64.6	72.2	49.7	65.5
Inspections of catalytic charge stock:				
Characterization factor.....	11.64	11.66	11.67	11.68
Sulfur, Braun-Shell, percent.....	2.42	2.40	2.30	2.28
Carbon residue, Conradson, percent, ASTM D189-46.....	1.40	1.65	0.40	0.75
Metals, p.p.m.:				
Vanadium.....	16.8	16.8	1	1
Nickel.....	1.6	2.5	0.1	0.3

Figure 2 of the accompanying drawings graphically illustrates the variation of metals content with yield of catalytic charge stock and shows the gain in yield by the process of the present invention (curve A) as compared with vacuum distillation of the same charge stock (curve B). Similar information is given in Table III which shows that a decrease in the vanadium content to 16.8; 10; 5 and 1 parts per million in accordance with the present invention results in an increase in yield of 7.6; 10; 12.3 and 15.8 percent respectively greater than vacuum distillation.

Table III

Vanadium content of catalytic charge stock, p.p.m.....	16.8	10	5	1
Yields, percent by volume on crude:				
Vacuum reduction.....	64.6	60	55.5	49.7
Distillation and solvent extraction.....	72.2	70.0	67.8	65.5

It will be apparent from the foregoing that it is possible to operate the present invention to obtain a larger yield of catalytic charge stock of a given metals content or to obtain a lower metals content for a given volume or boiling range. In the first case, larger ultimate yields of more valuable gasoline would result while in the second case more economical operation of the catalytic cracking operation would be possible because of the improvement in the selectivity of the catalyst. Also it is to be noted that the procedure of the present invention yields a catalytic cracking charge stock having a lower aromatic content so that yields of gasoline would be higher, since aromatic hydrocarbons give lower yields of gasoline and higher yields of coke during catalytic cracking. It will be apparent that the distillation to separate the high and low metals content fractions may be carried out in a conventional refinery distillation of a crude petroleum or fraction thereof which contains undesirable metals content and which is to be distilled to prepare a catalytic cracking charge stock. Also where the extracted higher boiling fraction alone or combined with the lower boiling fraction contains a metalliferous content higher than desired for catalytic cracking charge stock, it may be combined with a catalytic cracking charge stock having a lower metalliferous content to obtain a mixture having the desired characteristics.

I claim:

1. The process of catalytically cracking a charge stock which contains a metalliferous impurity in an amount sufficient to cause deterioration in selectivity of the cracking catalyst which comprises in combination subjecting the charge stock to distillation to separate a lower boiling portion which contains a smaller amount of metalliferous impurity than the original charge stock and an undistilled residual fraction which contains a larger amount of metal-

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liferous impurity than the original charge stock, extracting the undistilled residual fraction with a solvent having selectivity for aromatic hydrocarbons and subjecting the raffinate phase to catalytic cracking.

2. The process of catalytically cracking a charge stock which contains a metalliferous impurity in an amount sufficient to cause deterioration in selectivity of the cracking catalyst which comprises in combination subjecting the charge stock to distillation to separate a lower boiling portion which contains a smaller amount of metalliferous impurity than the original charge stock, and an undistilled residual fraction which contains a larger amount of metalliferous impurity than the original charge stock, extracting the undistilled residual fraction with a solvent selected from the group consisting of furfural, acetonitrile, dimethyl formamide, dimethyl sulfoxide and mixtures thereof and subjecting the raffinate phase to catalytic cracking.

3. The process of catalytically cracking a gas oil which contains a metalliferous impurity in an amount sufficient to cause deterioration in selectivity of the cracking catalyst which comprises in combination subjecting the gas oil to distillation to separate a lower boiling portion which contains a smaller amount of metalliferous impurity than the original gas oil and an undistilled residual fraction which contains a larger amount of metalliferous impurity than the original gas oil, extracting the undistilled residual fraction with a solvent selected from the group consisting of furfural, acetonitrile, dimethyl sulfoxide, dimethyl formamide and mixtures thereof, separating occluded solvent from the raffinate phase, combining the raffinate phase with the above mentioned lower boiling fraction and subjecting the combination to catalytic cracking.

4. The process of catalytically cracking a charge stock which contains a member of the group consisting of vanadium and nickel impurities in an amount sufficient to cause deterioration in selectivity of the cracking catalyst which comprises in combination subjecting the charge stock to distillation to separate a lower boiling portion which contains a smaller amount of said metalliferous impurity than the original charge stock and an undistilled residual fraction which contains a larger amount of said metalliferous impurity than the original charge stock, extracting the undistilled residual fraction with a solvent selected from the group consisting of furfural, acetonitrile, dimethyl sulfoxide, dimethyl formamide and mixtures thereof, separating occluded solvent from the raffinate phase combining the raffinate phase with the above mentioned lower boiling fraction and subjecting the combination to catalytic cracking.

5. The process of catalytically cracking a gas oil which contains a member of the group consisting of vanadium and nickel impurities in an amount sufficient to cause deterioration in selectivity of the cracking catalyst which comprises in combination subjecting the gas oil to distillation to separate a lower boiling portion which contains a smaller amount of vanadium or nickel impurity than the original charge stock and an undistilled residual fraction which contains a larger amount of vanadium or nickel impurity than the original charge stock, extracting the undistilled residual fraction with furfural, removing furfural from the raffinate phase, combining the raffinate phase with the above mentioned lower boiling fraction and subjecting the combination to catalytic cracking.

6. The process of catalytically cracking a wide boiling range gas oil which contains a member of the group consisting of vanadium and nickel impurities in an amount sufficient to cause deterioration in selectivity of the cracking catalyst which comprises in combination subjecting the gas oil to distillation to separate a lower boiling portion which contains less than about one part per million of said impurity and an undistilled residual fraction containing a larger amount of said impurity, extracting the undistilled residual fraction with between about 0.25 and

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10 parts of furfural per part of gas oil at a temperature between about -10° F. and 250° F., removing furfural from the raffinate phase, combining the raffinate phase with the above mentioned lower boiling fraction and subjecting the combination to catalytic cracking.

References Cited in the file of this patent

UNITED STATES PATENTS

2,028,121 Cottrell ----- Jan. 14, 1936
 2,146,039 Whiteley ----- Feb. 7, 1939
 2,228,510 Dearborn et al. ----- Jan. 14, 1941

2,429,875
 2,510,673
 2,608,470
 2,793,167
 5 2,793,168
 2,834,715

8

Good et al. ----- Oct. 28, 1947
 Annable ----- June 6, 1950
 Helmers et al. ----- Aug. 26, 1952
 Webber ----- May 21, 1957
 Corneil et al. ----- May 21, 1957
 Pratt ----- May 13, 1958

OTHER REFERENCES

Wrightson: Analytical Chemistry, vol. 21, No. 12,
 10 December 1949, pp. 1543-1545.