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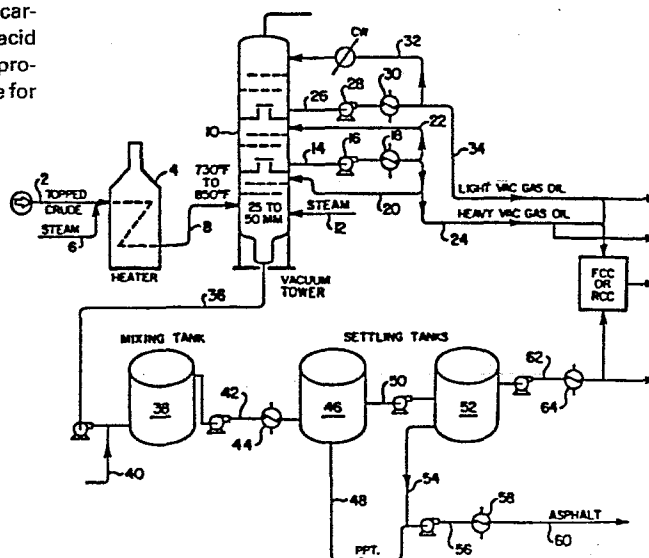
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(54) Combination process for upgrading crude oil including demetallizing and decarbonizing thereof.

(57) The invention is concerned with upgrading crude oil by zeolite catalytic cracking and particularly the residual portion of atmospheric distillation or that portion of crude oil boiling above about a middle distillate fraction after treatment by the combination of vacuum distillation, demetallizing and decarbonizing a vacuum resid portion with concentrated acid thereby concentrating metal contaminants in an asphalt product thereof separated from a liquid product more suitable for catalytic upgrading with vacuum gas oil.



A COMBINATION PROCESS FOR UPGRADING CRUDE OIL
INCLUDING DEMETALLIZING AND DECARBONIZING THEREOF

BACKGROUND OF THE INVENTION

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FIELD OF THE INVENTION

The invention is concerned with upgrading crude oil by zeolite catalytic cracking and particularly the residual portion of atmospheric distillation or that portion of crude oil boiling above about a middle distillate fraction after treatment by the combination of vacuum distillation, demetallizing and decarbonizing a vacuum resid portion with concentrated acid thereby concentrating metal contaminants in an asphalt product thereof separated from a liquid product more suitable for catalytic upgrading with vacuum gas oil.

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DESCRIPTION OF THE PRIOR ART

In general, gasoline and other liquid hydrocarbon fuels boil in the range of about 38°C (100°F) to about 343°C (650°F). However, the crude oil from which these fuels are made contains a diverse mixture of hydrocarbons and other compounds which vary widely in molecular weight and therefore boil over a wide range. For example, crude oils are known in which 30 to 60% or more of the total volume of oil is composed of compounds boiling at temperatures above 343°C (650°F). Among these are crudes in which about 10% to about 30% or more of the total volume consists of compounds so heavy in molecular weight that they boil above 552°C (1025°F) or at least will not boil below 552°C (1025°F) at atmospheric pressure.

Because these relatively abundant high boiling components of crude oil are unsuitable for inclusion in gasoline and other liquid hydrocarbon fuels, the petroleum refining industry has developed processes for cracking or breaking the molecules of the high molecular weight, high boiling compounds into smaller molecules which do boil over appropriate liquid fuel boiling range. The

cracking process which is most widely used for this purpose is known as fluid catalytic cracking (FCC). Although the FCC process has reached a highly advanced state, and many modified forms and variations have been developed, their unifying factor is that a vaporized hydrocarbon feedstock is caused to crack at an elevated temperature in contact with a cracking catalyst that is suspended in the feedstock vapors. Upon attainment of the desired degree of molecular weight and boiling point reduction the catalyst is separated from the desired products.

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Crude oil in the natural state contains a variety of materials which tend to have quite troublesome effects on fluid catalytic cracking processes. Among these troublesome materials are coke precursors (such as asphaltenes, polynuclear aromatics, etc.), heavy metals (such as nickel, vanadium, iron, copper, etc.), lighter metals (such as sodium, potassium, etc.), sulfur, nitrogen and others. Certain of these, such as the lighter metals, can be removed substantially by desalting operations, which are part of the normal procedure for pretreating crude oil for fluid catalytic cracking. Other materials, such as coke precursors, asphaltenes and the like, tend to break down into coke during the cracking operation, with deposits of coke on the catalyst impairing contact between the hydrocarbon feedstock and the catalyst, and generally reducing the catalyst selectivity and/or activity level. The heavy metals of nickel, vanadium, iron and copper concentrated in a 343°C (650°F) plus feed portion transfer almost quantitatively from the feedstock to the catalyst surface.

If the catalyst is reused again and again for processing additional feedstock, which is usually the case, the heavy metals accumulate on the catalyst to the point that they unfavorably alter the composition of the catalyst and/or its catalytic effect upon the feedstock. For example, vanadium tends to form fluxes with certain

components of commonly used FCC catalysts, lowering the melting point of portions of the catalyst particles sufficiently so that they begin to sinter and become ineffective cracking catalysts. Accumulations of vanadium and other heavy metals, especially nickel, are considered "poison" to the catalyst. They tend in varying degrees to promote excessive dehydrogenation and aromatic condensation, resulting in excessive production of carbon and gases with consequent impairment of liquid fuel yield. A crude oil and residual fractions of crude oil or other heavy oil sources that are particularly abundant in these metal contaminants exhibit similar behavior. Such heavy oil fractions also comprise relatively large quantities of coke precursors, referred to in the prior art as metallo-organic compounds or as carbo-metallic containing oils. Such heavy residual oil feeds represent a particular challenge for upgrading to liquid fuel products by the petroleum refiner.

In general, the coke-forming tendency or coke precursor content of an oil fraction can be ascertained by determining the weight percent of carbon remaining after a sample of that oil has been pyrolyzed. The industry accepts this value as a measure of the extent to which a given oil tends to form non-catalytic coke when employed as feedstock in a catalytic cracker. Two established tests are recognized, the Conradson Carbon and Ramsbottom Carbon tests, the former being described in ASTM D189-76 and the latter being described in ASTM Test No. D524-76. In conventional FCC practice, Conradson carbon values on the order of about 0.05 to about 1.0 are regarded as indicative of acceptable feed. The present invention is particularly concerned with the use of petroleum hydrocarbon feedstocks and residual portions thereof which provide relatively high Conradson carbon values and thus exhibit substantially greater potential for coke formation than lower boiling gas oil feeds.

The heavy metals content of an oil is often expressed in the prior art by the following formula (patterned after that of W. L. Nelson In Oil and Gas Journal, page 143, October 23, 1961) in which the content of each metal present is expressed in parts per million of such metal, as metal, on a weight basis, based on the weight of feed:

$$\text{Nickel Equivalents} = \text{Ni} + \frac{\text{V}}{4.8} + \frac{\text{Fe}}{7.1} + \frac{\text{Cu}}{1.23}$$

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According to conventional FCC practice, the heavy metal content of feedstock for FCC processing is controlled at a relatively low level, e.g. about 0.25 ppm Nickel Equivalents or less. The present invention is concerned with the processing of feedstocks containing metals substantially in excess of this value and which therefore have a significantly greater potential for accumulating on and poisoning catalyst.

In conventional FCC practice, in which circulating inventory of catalyst is used again and again in the processing of fresh feed, with periodic or continuing minor addition and withdrawal of fresh and spent catalyst, the metal content of the catalyst is maintained at a level which may for example be in the range of about 200 to about 600 ppm Nickel Equivalents. The process of the present invention is concerned with the use of equilibrium catalyst having a substantial metals content up to 5000 or 6000 ppm of Ni + V or higher and which therefore has a tendency to promote dehydrogenation, aromatic condensation, gas production and/or coke formation. Therefore, high metals accumulation on catalyst is normally regarded as quite undesirable in FCC processing.

There has been a long standing interest in the conversion of carbo-metallic containing heavy oil fractions to form gasoline and other liquid fuels. Several proposals involve treating the heavy oil

feed to remove the metal therefrom prior to cracking, such as by hydrotreating, solvent extraction and complexing with Friedel-Crafts catalysts, but these techniques have been criticized as unjustified economically. Another proposal employs a combination cracking
5 process having "dirty oil" and "clean oil" units. Still another proposal blends residual oil with gas oil and controls the quantity of residual oil in the mixture in relation to the equilibrium flash vaporization temperature at the bottom of a riser hydrocarbon conversion zone employed in the process. Still another proposal
10 subjects the feed to a mild preliminary hydrocracking or hydrotreating operation before it is introduced into the cracking unit. It has also been suggested to contact a carbo-metallic containing oil feed such as residual or reduced crude oils with hot taconite pellets to produce gasoline. This is a small sampling of the
15 many proposals which have appeared in the patent literature and technical reports. Various other methods for removing metal contaminants or carbo-metallic compounds from the heavy oil portion of crude oils have been suggested in the prior art. Some of these are as follows:

20 Powell 2,778,777 - Crude oils are treated with a 10% sulfuric acid solution and then with an alkaline solution to form metal compounds soluble in a water phase for removal from the oil phase.

25 Erdmond 3,190,829 removes heavy metals from petroleum oils by treating with methyl or ethyl sulfonic acids.

30 Adams 3,245,902 removes nickel and vanadium from petroleum fractions by treatment with hydrofluoric acid at a temperature in the range of 121°C-191°C (250-375°F) for 10 to 60 minutes.

Schulze 4046687 is concerned with treating aqueous solution of arsenic, antimony and bismuth with a water insoluble or low solubility salt of phosphoric acid or an ester thereof.

- 5 Blytas 4048061 uses acidified active carbon to remove lead, copper, nickel, vanadium and iron.

- 10 Kluksdahl 4192736 relies upon alumina promoted with phosphorous oxide to remove nickel and vanadium from petroleum resid.

Gould 4197192 uses an organic peroxyacid to oxidize a petroleum feed to remove vanadium and nickel.

- 15 Some crude oils are relatively free of coke precursors or heavy metals or both, and the most troublesome components of crude oil are for the most part concentrated in the highest boiling fractions. Accordingly, it has been possible heretofore to largely avoid the problems of coke precursors and heavy metals by sacrificing the liquid fuel yield which would be potentially available from the highest boiling vacuum resid fraction comprising the metal contaminants and substantial Conradson Carbon. More particularly, conventional FCC practice has employed as feedstock that fraction of crude oil which boils in the range of at about 343°C (650°F) to about 538°C (1000°F). Such fractions are relatively free of Conradson carbon, coke precursors and heavy metal contamination. Such feedstock, known as "vacuum gas oil" (VGO) is generally prepared from crude oil by distilling off the fractions boiling below about 343°C (650°F) at atmospheric pressure and then separating the 343°C (650°F) plus fraction by vacuum distillation from the heavier resid fraction as vacuum gas oil boiling between about 343°C (650°F) up to about 482°C (900°F) or 552°C (1025°F).
- 20
- 25
- 30

The vacuum gas oil plus atmospheric gas oils is used as the oil feedstock in conventional FCC processing. The heavier resid fraction of vacuum distillation is normally employed for a variety of other purposes, such as for instance the production of asphalt, #6 fuel oil, or used as marine Bunker C fuel oil. The present invention is concerned with recovering a partially demetallized portion of these heavier oil fractions containing substantial quantities of both coke precursors and heavy metals contaminants as well as other troublesome components. The recovery partially demetallized resid portion of vacuum distillation is then used with a lower boiling gas oil fraction thereby increasing the volume of charge oil whereby an increased overall yield of gasoline and other hydrocarbon liquid fuels may be realized from a given quantity of crude oil.

The oil feeds capable of being catalytically cracked following the acid treatment of this invention are those which include at least about 70 percent of which boil above 343°C (650°F) and contain a carbon residue on pyrolysis and up to about 4 parts per million of nickel equivalents of heavy metals. Examples of these oil feeds are fractions of crude oils such as topped crudes, residual or reduced crudes, residua, and extracts from solvent de-asphalting. The unusually large amount of coke which deposits on the catalyst in carbo-metallic oil processing presents critical problems, the primary problem arising from the fact that the reactions in the regenerator which convert coke to water, carbon monoxide and carbon dioxide are highly exothermic. Using a carbo-metallic feed with its unusually high content of coke precursors as compared to gas oil FCC feeds, can substantially increase the amount of coke to be burned in the regenerator and thus the regeneration temperatures can become excessive if there is thorough burning of deposited coke. Excessive regeneration temperatures can permanently deactivate the catalyst and/or damage the regenerating equipment.

The heat of combustion of coke depends upon the concentration of hydrogen in the coke and the ratio of CO_2 to CO in the products of combustion. Carbon produces 13,910 BTU per pound when burned to CO_2 and only 3,962 BTU per pound when burned to CO. Hydrogen produces 61,485 BTU per pound when burned to H_2O . The heats of combustion of coke for three representative levels of hydrogen and four different ratios of CO_2/CO are given in the following table:

10

TABLE IHeat of Combustion BTU/lb Coke

15

CO_2/CO Ratio	<u>Percent Hydrogen</u>		
	2	4	6
0.5	8,362	9,472	10,582
20 1.0		11,038	12,083
3.0			14,446
4.0	12,912		14,894

The problems encountered in regenerating catalysts coated with a high concentration of coke may be aggravated when catalysts of the crystalline zeolite or molecular sieve type are used. These catalysts, which are crystalline aluminosilicates made up of tetracoordinated aluminum atoms associated through oxygen atoms with silicon atoms in the crystalline structure, are susceptible to a rapid loss of cracking activity by accumulated metal contaminants upon extended exposure to high temperatures. Therefore, any economically acceptable method for reducing deposited metal

contaminants and Conradson carbon is considered an advance in the industry.

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Summary of the Invention

Accordingly one object of this invention is to provide a method for converting carbo-metallic containing residual oils to liquid fuels.

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Another object is to provide a carbo-metallic containing residual oil conversion process which effectively reduces the temperatures encountered in the provided catalyst regeneration operation.

15

It is still another object to provide a carbo-metallic containing residual oil conversion process wherein substantial quantities of metal contaminants and Conradson carbon are removed from a portion of vacuum resid passed to catalytic cracking.

20

In accordance with one further aspect of this invention, the metal contaminants in the crude oil fraction to be upgraded are removed as a function of two variables. The variables are (1) oxidation of a chelated metals to give a water soluble metal and (2) precipitation of asphaltenes and/or aromatic materials with which the metals are chelated. By effecting metal contaminant removal as herein provided, the amount of heavy hydrocarbon material removed from the feedstock is in the range of 0.1% to 20% by weight depending on the feed stock being processed. The metals removal accomplished by the method of this invention includes from 15% up to 82% nickel; from 5% up to 95% vanadium and about 50%± 10% iron.

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More particularly, there is added to a given amount of a heavy oil fraction from 0.5 to 2.0% (weight/weight) of a concentrated acid

such as 85% phosphoric acid, concentrated sulfuric and nitric acid. The mixture thus formed of the heavy oil fraction and phosphoric acid is heated to a temperature of at least 66°C (150°F) and preferably from about 104°C to 177°C (220°F to 350°F) for a period
5 of time sufficient for reaction to occur. During heating of the formed mixture an organo metal complex is formed with contaminants and asphaltenes which precipitate out. The thus treated heavy oil fraction is then separated from the precipitate at the temperature at which it is formed. This procedure produces a heavy oil fraction
10 with a lower metals content of lower Ramsbottom carbon value, the density of the heavy oil fraction is thus improved and the crackability of the thus treated resid heavy oil portion to form liquid transportation fuels is greatly enhanced. The substantial metals removal accomplished by the method and process of this
15 invention substantially improves the cracking catalyst on stream life by reducing the rate of metals deposition thereon.

A BRIEF DESCRIPTION OF THE DRAWINGS

20 The drawing is a schematic flow diagram of a preferred system for practicing the invention.

DISCUSSION OF SPECIFIC EMBODIMENTS

25 Referring now to the drawing, a topped crude oil fraction obtained from the bottom of an atmospheric distillation tower is charged to the combination process of this invention. The topped crude is separated from an atmospheric distillation tower (not
30 shown) with an initial boiling point within the range of 316°C to 371°C (600 to 700°F) and more usually about 343°C (650°F). The thus obtained topped crude is charged by conduit 2 to furnace 4. Stream is charged by conduit 6 for admixture with the heavy

residual portion of the crude oil in conduit 2 to reduce coking thereof within the furnace tubes during heating thereof to a temperature within the range of about 388°C (730°F) up to about 454°C (850°F) before discharge by conduit 8 into a lower bottom portion of a vacuum distillation tower 10. A pressure is maintained within a bottom portion of tower 10 within the range of 25 to 50 mm of Hg. Steam is added to the tower 10 by conduit 12 to assist with obtaining separation of light and heavy vacuum gas oils from the residual oil to topped crude fraction charged to tower 10. A heavy gas oil fraction is withdrawn by conduit 14 from a tray within tower 10, passed to pump 16 for passage to heat exchange 18. Thereafter a portion of the heavy vacuum gas oil is recycled to the tower by conduit 20, another portion thereof is recycled by conduit 22 to the tower 10 and a portion is withdrawn by conduit 24 for use as discussed below.

A light gas oil fraction is withdrawn from an upper liquid accumulation tray in tower 10 by conduit 26 for passage to pump 28 and heat exchanger 30. A portion of the withdrawn light cycle oil or light vacuum gas oil is recycled to an upper portion of tower 10 as reflux by conduit 32. Another portion is withdrawn by conduit 34 for use as discussed below.

A vacuum resid is withdrawn from the bottom of tower 10 by conduit 36 and passed to a mixing tank 38. Phosphoric acid of about 85% concentration is charged by conduit 40 to mixing tank 38 maintained after 104°C (220°F) after admixture with vacuum resid in conduit 36. A weight ratio of resid to phosphoric acid in a range of 0.5 to 1 is maintained in mixing tank 38. The mixture formed in tank 38 is then passed by conduit 42 to heat exchanger 44 and thence to a first settling tank 46. A first precipitate comprising an organometallic phosphorous complex formed in settling tank 46 maintained at a temperature of at least 104°C (220°F) up to about

177°C (350°F) is collected in the bottom of the tank. Means are provided in the bottom of tank 46 for scraping or otherwise providing for removal of the asphaltic precipitate as by conduit 48 for passage to asphalt processing. A portion of the material charged to tank 46 and not completely reacted to form the metal complex precipitate is passed from tank 46 by conduit 50 to a second settling tank 52. Tank 52 is maintained at a temperature of at least 104°C (220°F) wherein an additional metal complex asphaltic precipitate is formed and which settles to the bottom of the tank. Means are provided in the bottom of the tank for collecting and removing the formed precipitate as by conduit 54. The precipitates removed by conduits 48 and 54 are joined together and passed by conduit 56 to a heat exchanger 58 providing heat sufficient to maintain the precipitate phase fluid for passage by conduit 60 to asphaltic material processing.

The vacuum resid thus treated to remove metal contaminants and some asphaltenes along with some Conradson carbon or Ramsbottom carbon producing components is withdrawn from tank 52 by conduit 62 comprising heat exchanger 64 for passage to a fluid catalyst cracking unit (not shown) along with vacuum gas oils recovered by conduits 24 and 34 as above discussed.

A reduced crude or vacuum resid treated as herein described, provides a partially demetallized and decarbonized feed or heavy oil fraction more suitable for catalytic cracking beneficiation. Thus in one specific example in which 0.895% phosphoric acid was added to the resid fraction, removed 5.06% of material from the feed. Of this removed material, 58.33% is hexane insolubles and 0.18% THF insolubles. Processing by catalytic cracking such acid treated material admixed with atmospheric and vacuum gas oils boiling above about 288°C (550°F) provides a feed suitable to obtain an increase of 18.34 vol % of gasoline and a 19 percent reduction in coke make.

The metals removal capability and feed conversion attributed to the method and process of the invention is represented by the following data.

5 In Table 1 below an equilibrium zeolite cracking catalyst identified as Davision GRZ-1 and used in the process of this invention is identified in substantial measure. Table 1 also provides a comparison of the catalyst before and after acid treatment particularly with phosphoric acid and the effect of
10 subsequent catalyst regeneration in the catalyst processing activity.

 In preparing the results of Figure 1, an equilibrium catalyst (GRZ-1 and described in the Table) is used in a cracking operation in which highly contaminated, carbon contaminated residual
15 feedstock, (a heavy vacuum gas oil prepared in apparatus as described in the Figure but deleting all elements numbered higher than 40) is fed to a conventional fluid catalytic cracking apparatus in which the catalyst circulates between a riser cracking zone and a regeneration zone in which carbon is removed by oxidation. The
20 phosphoric acid is mixed with the vacuum tower bottoms as shown in the Figure and the mixture then moves (without the need for mixing tank 38 which may optionally be provided) directly into the FCC or RCC unit shown at the right-hand side of the drawing. The phosphoric acid will generally be of the commercial 85%
25 concentration but may be of lower or higher concentration and may be premixed with a small amount of emulsifying agent and oil to aid in dispersion. The phosphoric acid: vacuum bottoms weight ratio is 0.01 in the tests shown in Table 1. This ratio will preferably be in the range of about 0.001 to about 0.05, more preferably from
30 about 0.003 to about 0.03 and most preferably from about 0.005 to about 0.015 weight ratio.

In this embodiment of the invention, phosphoric acid is not the only acid which may be used. Instead, other acids, e.g., sulfuric acid (either oleum or lower concentration of H_2SO_4), or other strong mineral acid may be utilized though nitric and hydrohalic acids will be less preferred because of their contaminating nitrogen and halogen anions which can cause damage to the catalyst and/or apparatus. Acidic acid may also be employed in place of phosphoric acid as the principal objective is to provide regeneration of acid sites on the zeolite in the catalyst material. The zeolite is embedded in an inorganic matrix which can be readily penetrated by the acids and contact between the acid and the zeolite though not wishing to be bound by any theory, apparently the combination presence of the zeolite, the inorganic matrix, e.g., alumina or silica and the acid acts to provide composite molecules in the inorganic matrix which molecules provide acid sites. These acid sites excellerate the cracking of the heavy molecules contained in the vacuum tower bottoms or other residuums being processed. This cracking provides products of smaller molecular weight which can then enter through the inorganic matrix and contact the zeolite portion of the catalyst contained within the matrix. Upon contact between the vapor and the zeolite, further cracking occurs and the final products are largely in the valuable transportation fuel range of boiling points, e.g. light cycle oil, gasoline, and C3-C4 hydrocarbons.

25

TABLE 1Catalyst And Effect Of Acid On The Catalyst

5	<u>Catalyst</u>	Equilibrium	Zeolite	Cracking	Catalyst	(Davison
	GRZ-1)					
	Surface Area (m ² /g)			93		
	Pore Vol. (cc/g)			0.23		
10	Metals (ppm)		11000 Ni & V	(0.86%V; 0.24% Ni; 0.36% Fe)		
	<u>Catalyst</u>					
		Rel.	Vol.%	Wt.%	Wt.%Sel.	
		<u>Act.</u>	<u>Conv.</u>	<u>Conv.</u>	<u>To C5-430°F</u>	<u>CPF</u> <u>HPF</u>
15	GRZ-1 Untreated	55.1	69.71	65.46	75.02	0.918 3.115
	GRZ-1 Treated	64.2	71.07	66.19	75.81	0.866 3.390
	CPF = Carbon Producing Factor HPF = Hydrogen Producing Factor					

20 Table 2 on the other hand identifies a feed stock processed by the method of the invention and identified as 735 tank (2/7/81). The feed is a mixed composition of crude oil as identified.

TABLE 2

Feedstock Analysis
735 Tank Reduced Crude

5	Date	<u>2/7/81</u>
	API	20.0
	Sulfur, WT %	2
	Distillation: 5%	555
10	10%	612
	20%	680
	30%	723
	40%	765
	50%	818
15	60%	875
	70%	938
	80%	991
	CRX @ 1000	
20	Vis, cs @ 99°C (210°F)	10.5
	Ramsbottom Carbon, WT %	7
	Basic Nitrogen, ppm	560
	Total Nitrogen, ppm	1900
	Heptane Insolubles, %	2.7
25	Metals:	
	Iron, ppm	4
	Nickel, ppm	17
	Vanadium, ppm	65
	Sodium, ppm	1
30	Copper, ppm	<1

2/7/81 - 38.5% VGO, 31.5% ABL, 15.2% Mayan, 14.8% ITHM

Table 3 presented below identifies the yields obtained when processing by catalytic cracking the feedstock of Table 2 with and without acid treatment.

TABLE 3

Product Distribution And Feedstock Crackability

5	<u>Test # And Feed</u>	PDU 126*		PDU 168**	
	<u>Conditions</u>				
	Temp °F	1000		1000	
10	Cat/Oil wt./st	6.8		6.54	
	RX Atmos.	5% Steam		5% Steam	
	WHSV	17.74		18.34	
	<u>Products Dist.</u>	<u>Wt%</u>	<u>Vol%</u>	<u>Wt%</u>	<u>Vol%</u>
15	H ₂	0.98		0.21	
	C ₁	1.92		1.53	
	C ₂ 's	2.93		2.39	
	C ₃	3.16	5.82	3.47	6.47
20	C ₃ =	5.55	9.98	4.79	8.70
	iC ₄ =	7.27	12.10	8.76	14.76
	iC ₄ = + 1-C ₄ =	2.23	3.48	1.58	2.49
	nC ₄	2.28	3.65	2.57	4.17
	(c) 2-C ₄ =	0.97	1.45	0.76	1.15
25	(t) 2-C ₄ =	1.36	2.09	1.10	1.71
	CO, CO ₂ , COS, H ₂ S	0.85		0.60	
	C ₅ -221°C (430°F)	33.37	43.95	38.93	52.01
	221°C-332°C (430-630°F)	11.74	12.46	13.14	14.61
	>332°C (>630°F)	10.05	9.28	7.78	7.78
30	Coke	15.33		12.40	

TABLE 3 (Continued)

	Conv. of >221°C (>430°F), Vol. %	78.26	77.61
	Sel. C ₅ -221°C (430°F), Vol. %	56.16	67.01
5	<u>Product Characterization</u>		
	H ₂ /C ₁	0.51	0.14
	Total C ₃ 's, (Paraffin:Olefin)	15.80, (0.58)	15.17, (0.74)
	Total C ₄ 's, (Iso:Normal)	22.77, (1.64)	24.28, (1.97)
	<u>C₅-221°C (430°F) Fraction</u>		
10	RONC	93.4	92.1
	Br. No.	18.5	14.7
	%SAT./OLEF./AROM.	38.0/7.8/54.2	44.0/4.4/51.2
	<u>221°C-332°C (430-630°F) Fraction</u>		
	Br. No.	7.5	6.2
15			
	Total Gasoline + LCO, Vol%	56.41	66.62
	Total Slurry + Coke, Wt%	25.38	20.18
	LCO:HCO Ratio, Wt%	1.17	1.69

20 *(38.5% VGO, 31.5% ABL, 15.2% Mayan, 14.8% ITHM)

**Treated with 0.104 moles of conc. H₃PO₄ + Asphaltenes Removed.

The data presented in Table 3 above shows quite clearly the improved results obtained when practicing the method and concepts of the inventions. That is, the acid treated feed used in test PDU168 shows a lower C_3 - gas yield, an increased yield of C_5 -
5 221°C (430°F) gasoline product and higher selectivity, a higher yield of 332°C (630°F) - cycle oil and a lower coke and slurry oil (>332°C) (>630°F) yield. The data of Table 3 are substantially self explanatory with respect to the improvements obtained when
10 cracking acid treated feed to effect partical demetallizing and decarbonizing thereof over that obtained with a similar feed which has not been acid treated as herein provided.

Table 4 below is presented to show the effect of different acid percent treatment on different metal content feeds with respect to
15 metals content before and after acid treatment.

TABLE 4

735 Tank RCC Feed

5				Ni			
	<u>Treatment</u>	<u>%H₃PO₄</u>	<u>% ppt</u>	<u>ppm</u>	<u>% Removed, Ni</u>	<u>V, ppm</u>	<u>% Removed, V</u>
	Before	-	-	33	-	163	-
	After I	0.5	1.45	27	18	155	5
10	II	1.0	3.54	18	45.5	121	26

735 Tank RCC Feed

15	<u>Treatment</u>	<u>%H₃PO₄</u>	<u>% ppt</u>	<u>Ni, ppm</u>	<u>V, ppm</u>	<u>Fe, ppm</u>
	Before	0	-	17	65	4
	After	2.045%	18%	2	11	2
	%Removed			88	83.1	50

20 735 Tank ABL-ABM Reduced Crude

	<u>Treatment</u>	<u>%H₃PO₄</u>	<u>% ppt</u>	<u>Ni, ppm</u>	<u>V, ppm</u>	<u>Fe, ppm</u>
	Before	-		15	69	8
25	After	1.26	2.34	7	26	2
	%Removed			53.3	62.3	75

It is clearly evident from the data above presented that treating a resid portion of a topped crude oil as herein provided to effect partial demetallizing and decarbonizing of the feed before effecting catalytic cracking thereof with the gas oil portion of the crude made substantial improvements in the zeolite cracking operation including improved product selectivity and yield.

Having thus generally described the method and process of this invention and provides examples in support thereof, it is to be understood that no undue restrictions are to be imposed by reasons thereof except as defined by the following claims. References cited herein, and literature they mention, are hereby incorporated by reference.

15 What is claimed is:

-23-

1. A method for reducing metal contaminants and carbon producing materials in a vacuum resid which comprises:
 - (a) mixing concentrated acid with vacuum resid in a mixing zone at a temperature sufficient elevated to maintain a liquid phase therein;
 - (b) passing the acid-vacuum resid liquid phase from the mixing zone to a settling operation wherein a reaction precipitate of an organometallic-acid complex is settles out from said liquid phase; and
 - (c) recovering said liquid phase supported from reaction precipitate for use in a fluid catalyst cracking operation.
2. The method of claim 1 wherein the acid mixed with said vacuum resid is within the range of 0.5 to 1.0% on a weight basis and wherein the temperature is maintained during said mixing and settling operation with the range of 66°C (150°F) to about 177°C (350°F).
3. The method of claim 1 wherein the temperature of said mixing and settling operation is at least 104°C (220°F) and for a time sufficient to form said reaction precipitate between acid and resid to form said organometallic-acid complexes and wherein the liquid phase separated from precipitate is mixed with the gas oil product of a topped crude oil and subjected to crystalline zeolite fluid catalytic cracking under conditions to form gasoline and light cycle oil.
4. The method of claim 1 wherein the acid employed is phosphoric acid.
5. The method of claim 1 wherein said reduced crude comprises vacuum resid.

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6. A method for upgrading a topped crude oil boiling above about 260°C (500°F) which comprises:
- (a) separating atmospheric and vacuum gas oils from a topped crude and recovering a vacuum resid fraction therefrom;
 - 5 (b) contacting said vacuum resid in liquid phase with a quantity of phosphoric acid sufficient to form a precipitate therewith of an organometallic-phosphorous complex, separating said precipitate from said liquid phase;
 - 10 (c) mixing said liquid phase separated from precipitate with said atmospheric and vacuum gas oils to form a demetallized acid decarbonized mixed feed; and
 - 15 (d) catalytic cracking said mixed feed with a crystalline zeolite cracking catalyst under conditions providing increased yield of liquid gasoline product at a reduced coke make.
7. A method for reducing the deactivating effects of metal contaminants and Conradson carbon producing components of a topped crude oil upon a crystalline zeolite containing cracking catalyst in the production of gasoline which comprises:
- 20 (a) separating a heavy residual oil fraction from said topped crude comprising a high concentration of metal contaminants of nickel, vanadium, iron and Conradson carbon contributing material;
 - 25 (b) contacting said separated heavy residual oil with phosphoric acid of a concentration of at least 80% at a

temperature to form an organometallic precipitate therewith, separating said precipitate from said heavy residual oil; and

5 (c) catalytic cracking said heavy residual oil separated from said precipitate with a crystalline zeolite cracking catalyst under conditions producing gasoline and light cycle in combination with reduced yields of slurry oil and coke.

8. In a method for the catalytic cracking of nitrogen containing hydrocarbon feedstocks wherein the feedstock is contacted with
10 a catalyst under catalytic cracking conditions at elevated temperatures, the improvement comprising adding to said feedstock immediately prior to contact with said catalyst an amount of acid selected from the group consisting of sulfuric, hydrochloric, nitric, phosphoric and acetic acids sufficient to
15 neutralize a substantial portion of the basic nitrogen components contained in said feedstock.

9. The method of claim 8 wherein said feedstock contains at least 0.05 weight percent basic nitrogen and from about 0.1 to 5 weight percent, (based on total oil feed), acid is added to
20 achieve neutralization thereof and wherein said catalyst comprises a crystalline zeolite dispersed in an inorganic oxide matrix and wherein said zeolite comprises rare earth exchanged type Y zeolite and wherein said inorganic matrix is selected from the group consisting of silica, alumina, silica-alumina, silica magnesia hydrogels, silica sols, silica-alumina sols,
25 alumina sols, clay and mixtures thereof.

10. The method of claim 9 wherein said catalyst contains from about 1 to 30 percent by weight of an SOx control agent

selected from the group consisting of aluina, and rare-earth alumina composites.

