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THERMAL CRACKING IN AN OXYGEN FREE ATMOSPHERE

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This invention is directed to the conversion of crude
residua, asphaltenes, aromatic tars, and the like usually
having initial boiling points of about 650° F.+ to low
sulfur, low metals, lower boiling 430° F.+ gas oil hydro-
carbons by the noncatalytic liquid-phase thermal depoly-
merization of such residua in the presence of an organic
solvent (boiling range 150 to 800° F.) at temperatures of
about 650 to 900° F. substantially in the absence of avail-
able (molecular) oxygen for residence times of 0.5 to 6.0
hours.

More particularly, the present invention is concerned
with the upgrading of petroleum oils, particularly heavy
high boiling oils such as vacuum residua, to prepare there-
from low sulfur containing, low metals containing, bulk
gas oil having a boiling range of about 430° F.+ (usu-
ally 430° F. to 1100° F.) by liquid phase, thermal, non-
catalytic, nonhydrogen donor diluent cracking of the feed
in the presence of a monocyclic, bicyclic, or tricyclic aromatic
solvent and essentially in the absence of oxygen, viz.
<0.1 wt. percent oxygen to reduce the molecular weight
thereof and obtain higher value, more useful gas oils of
low metals and low sulfur content per gallon and emi-
nently suited as feedstock to catalytic cracking and hy-
drocracking operations.

The present invention in its essential features comprises
the following steps. First, the virgin residua feed is
blended at temperatures of 200 to 450° F. with a solvent
(preferably an aromatic solvent having a boiling point
range of about 400 to about 600° F.) in the absence of
oxygen. Then the blend of feed residua plus solvent is
heated at a temperature of about 650 to 900° F. for from
0.5 to 6.0 hours and usually 0.5 to 4 hours. This time
period is the average residence time for which the residua
feed is subjected to these temperatures in the presence of
the solvent. Then the heat-soaked blend is filtered using
any conventional filtration system to remove metals, sul-
fur, carbonaceous solid materials, etc. Following the fil-
tration step, the filtered blend (solution) is fractionally
distilled to obtain a small amount of naphthas and gasoline
fractions as a top stream; a side stream composed of the
initial solvent; and a bottom stream (main product) com-
posed of the lower molecular weight hydrocarbon gas oils
having a usual boiling point range of 430 to 1000° F. with
a significantly reduced sulfur and metals content.

An important process feature of this invention is that
the blend of feed and solvent should not be heated at the
above temperatures, 650 to 900° F. in the absence of the
solvent for longer than 30 minutes and preferably no
longer than 10 minutes at these temperatures during the
fractional distillation and/or processing steps. In other
words, the blend of solvent and converted feed during the
distillation step should be heated for no more than 30
minutes as the solvent is being separated from the con-
verted product. Failure to observe this process feature
will result in coke formation and reversal of the de-
polymerization process.

In accordance with this invention, various high molecu-
lar weight sulfur containing and metal containing virgin

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residua feeds, which can be the bottoms from crude oil
distillation and/or conversion processes, can be employed
as feeds for the instant process. Exemplary feedstock
materials to the present process can be: atmospheric
residua and vacuum residua; asphaltenes; aromatic tars;
coal tars; shale oils; heavy synthetic oils; natural tars and
asphalts; aromatic extracts; cycle stocks; pitches; and the
like. These materials can be liquids or solids at room
temperature and usually possess API gravities of -8°
to +30°, molecular weights of 200 to 20,000 and initial
boiling points above 650° F. Particularly preferred feed-
stocks, which can be employed in accordance with this in-
vention, are heavy residua characterized by API gravities
of 0° to 20°, molecular weights of 400 to 6000 and initial
boiling points above about 950° F.

In accomplishing the process of this invention, the sul-
fur-containing metals-containing, high molecular weight
feedstock is blended usually with an aromatic solvent in a
volume ratio of about 0.5:1 to 5:1 (volumes of aromatic
solvent per volume of residua feedstock). During the
blending step the solvent can be, and preferably is, heated
to 200 to 450° F., preferably about 200 to 300° F., and
the system is blanketed with an inert gas, for example,
nitrogen, hydrogen, etc. The available (molecular) oxy-
gen content of the feedstock and solvent should be less
than 0.1 wt. percent, and preferably the feedstock and
solvent should contain less than 100 p.p.m. oxygen from
the onset until the completion of thermal depolymeriza-
tion. The blending of the feedstocks in the solvent is ac-
complished substantially in the absence of both available
oxygen (molecular), oxygen and oxygen containing com-
pounds which thermally release molecular oxygen in situ
during the heat treatment to form intimate blend of feed-
stock and solvent.

The blended solution of feed and aromatic solvent(s)
is then heated in the liquid phase essentially in the ab-
sence of oxygen at temperatures ranging from 650° F. to
900° F., usually at temperatures ranging from 650° F. to
about 850° F., and more preferably at temperatures rang-
ing from about 675° F. to 775° F. The heating is con-
tinued to allow an average residence time for which the
residual feed-solvent solution is subjected to these tem-
peratures in the presence of the solvent for time peri-
ods of 0.1 to 6 hours, usually 0.5 to 6 hours, and more
preferably from about 1 to 4 hours. During the thermal
depolymerization (heating) step, pressures ranging from
atmospheric pressure to about 2000 p.s.i.g. can be used.
Usually, however, the pressures employed range from
about 20 p.s.i.g. to 2000 p.s.i.g., and preferably from about
200 p.s.i.g. to 1600 p.s.i.g. with hydrogen being employed
to establish all or part of the pressure. At the higher
temperatures the pressure is adjusted upwards to insure
the presence of the solvent in the liquid phase during ther-
mal depolymerization.

Subsequent to the thermal cracking step, the solution
containing the lower molecular weight gas oil product and
solvent is filtered using any conventional filtration sys-
tem, e.g. filters, centrifuge, settling tanks, etc. useful to
separate solid residues, such as metals, sulfur, carbona-
ceous residues, etc., from the liquid portion of the product-
containing, solvent-containing stream. These metals, sul-
fur containing compounds, and carbonaceous solid ma-
terials removed by the above filtration step usually repre-
sent less than about 20% by weight solids based on the
original residua feed. The solids, removed by filtration
or centrifugation from the product containing stream prior
to fractional distillation, can be processed for recovery of

nickel, vanadium, sulfur compounds, and other metals present therein.

An alternate process procedure to aid in the complete removal of the metals and sulfur compounds consists in a primary separation of the 1000° F.+ unreacted product by either paraffinic solvent (C₃+ hydrocarbons) precipitation or vacuum flashing and by resolution of the 100° F.+ material in the recycle aromatic solvent either on the filter or in a mixing zone after the primary separation.

Subsequent to the filtration and/or primary separation step, the product containing stream is fractionally distilled to separate the starting solvent and the lighter overhead products including varying amounts of gasoline from the demetallized, desulfurized 430° F. to 1000° F. gas oil product.

The present invention is capable of attaining conversions from the lower value, high Conradson carbon residua feedstock to the higher value desulfurized, demetallized gas oils with yields as high as about 70 to 80%. This constitutes a significant improvement over the more complicated and expensive catalytic or hydrogen donor diluent cracking procedures. Thus, the present invention requires neither use of a catalyst, nor the regeneration and/or replenishment of a hydrogen donating solvent; and the benefits and advantages of the improved process of this invention require neither a catalyst nor replacement of hydrogen to the aromatic solvent.

Moreover, the demetallization secured by the present process is excellent. Thus, when the feed contains 150 or more p.p.m. metals, the metals content in the product stream usually is below 20 p.p.m.

Another outstanding feature of the present invention, as compared to a coking procedure, is a reduction in the sulfur content of the gas oil fraction. Thus, sulfur content reductions of from 2.4 wt. percent in the residuum feed to the process to from 1.0 to 1.5 wt. percent in the gas oil product stream can be readily achieved in accordance with this invention.

A wide variety of solvents can be employed in accordance with the present invention. Preferably, however, the solvents employed are aromatic and more preferably naphthenic in nature. Usually the boiling point range of the solvents employed in accordance with this invention lies within the range of about 150° F. to 800° F. Thus, such solvents as benzene; toluene; ortho-, meta-, and para-xylene; ethyl benzene, etc. can be used. Preferably, however, the solvents used in this invention have a boiling point range from about 400 to about 600° F., and preferably are the highly boiling monocyclic, bicyclic and tricyclic hydrocarbon aromatic solvents. Exemplary materials suitable for use in accordance with this invention include, but are not limited to, the following: naphthalene, alkyl substituted naphthalenes, such as methyl naphthalene, anthracenes, phenanthrene, tetralin, decalin, phenol, xylidine, toluidine, phenylene diamine, amino phenol, α -methyl naphthyl amine, α -naphthol, β -naphthol, and materials of a similar nature which can have a variety of substituents, said substituents being inert to the thermal cracking reactions involved to the extent that they do not interfere therewith. Mixtures of any two or more of the above solvents can be used.

According to a preferred embodiment of this invention following the fractional distillation step, the product stream bottoms, if not previously removed and taken in solution after the primary separation step, can be filtered to remove carbonaceous residue which can then be recycled back to the initial solvent dissolving step for further conversion of these higher molecular weight materials not converted on the initial pass through the process. With the abovementioned suitable solvents, thermal depolymerization occurs with very little coke formation. One special advantage of this preferred embodiment of the present invention resides in the fact that it enables the

metal components to be segregated (concentrated) in the filtered solids thus rendering more amenable the economic recovery of the metals and of the other materials sought to be recovered from the insolubles. This is particularly true with respect to nickel and vanadium. For example, the conversion of asphaltenes from Bachaquero crude to naphthas and gas oil with low coke production can be readily accomplished in accordance with this invention. The coke yields in successive operations were, e.g., 11% and 8% based on the asphaltene portion of the charge when thermal depolymerization was conducted at temperatures of 700 to 810° F. for 1 to 4 hours residence time on heat, using methyl naphthalene and tetralin as the solvents, and controlling the oxygen content during the processing at less than 100 p.p.m. Analyses of the insoluble residues removed by filtration and/or settling showed a high concentration of metals. The solid residues (insolubles) obtained by filtration and settling contained from 2.8 to 4.4 wt. percent vanadium. The Bachaquero crude from which these insolubles were obtained originally contained 2000 p.p.m. vanadium. The product gas oils (650° F.+) produced in the main product stream had only 1 to 16 p.p.m. of vanadium and 0 to 4 p.p.m. nickel. This serves to further indicate the economically attractive nature of this invention.

Multiple staging of the thermal cracking step can be conducted in order to minimize any problems encountered during thermal depolymerization due to different rates of depolymerization of various feed and/or various components in the same feed. Different rates of depolymerization can cause some depolymerized products to be subjected to temperature conditions too high and for much longer than is ideally desirable. To counteract this, the thermal depolymerization can be conducted by use of two or more depolymerization stages in the same processing scheme, each operating at a different temperature and residence time for depolymerization. Thus, the readily depolymerizable materials are removed at relatively mild conditions and the more refractory materials removed at more severe conditions in absence of the products in the milder operation. In addition to varying the severity of temperature and time during the thermal depolymerization over the plurality of thermal depolymerization zones in the same depolymerization step, it is also possible to operate the various depolymerization zones using different aromatic solvents or mixtures of aromatic solvents; but in order to minimize the amount of recovery equipment necessary, use of the same solvent throughout the thermal depolymerization step is a preferred procedure.

The present invention will be illustrated in greater detail by the following illustrative examples.

Example 1

A charge of 300 grams of asphaltenes obtained from Bachaquero feed was dissolved in 300 grams of methyl naphthalene. This charge was found to contain no naphtha products boiling below 430° F. and no gas oil products boiling in the range of 484–1000° F. Of the 600 grams of total blended charge (blending being conducted at temperature of 300 to 400° F. for 10 minutes), 497.2 grams was used in thermal depolymerization (heat soaking) experiments. Some coke was formed, which was washed with methyl naphthalene, and the solvent was used in subsequent heat treatments. These heat treatments consisted of heating in an autoclave to about 810 to 820° F. for about 30 minutes, and then heating at 700 to 750° F. for about 3 hours. Oxygen was excluded from the system, and an oxygen-free blanket of hydrogen gas was employed to insure an oxygen-inert atmosphere. Maximum pressure in these runs was about 1200 p.s.i.g. Prior to the heat treatment, the autoclave was pressure tested with hydrogen at about 200 p.s.i.g. which was vented to atmospheric pressure at the start of the heating. Thus the heat soaking was conducted in the

presence of hydrogen at one atmosphere pressure. The heat soaking charges were as follows:

Run	Grams	Charge
A-----	178.7	Original solution.
B-----	179	Original solution.
C-----	171	88 grams of original solution plus 83 grams of methyl naphthalene obtained from the washing of coke of Run A.
D-----	171	51.5 grams of original solution plus 119.5 grams of methyl naphthalene obtained from washing coke from Runs B and C.

The coke-metal-sulfur insoluble product was removed from the main product by filtration using a Soxhlet thimble filter, and the combined coke product from Runs A, B, C, and D was extracted with benzene in a Soxhlet extractor to remove the residual product and methyl naphthalene. Benzene was removed by air drying on the filter. The combined products were distilled to remove the 430° F. and below products, and the bottoms were further distilled to demonstrate the presence of material other than methyl naphthalene. Of a still charge of 413 grams, 396 grams was higher boiling than 430° F. This material had the following distillation characteristics:

Volume, percent:	Temperature, ° F.
5 -----	451
10 -----	451
20 -----	458
30 -----	465
40 -----	478
50 -----	492
60 -----	492
70 -----	730
80 -----	841
90 -----	901
95 -----	925
Recov., percent -----	95
Res. -----	2

The methyl naphthalene employed was distilled in the range of 457 to 485° F. Hence, appreciable low boiling material resulted from the asphaltenes. These results, based on asphaltenes, are summarized in the table below in comparison with other results obtained wherein no solvent was employed.

Solvent	Methyl Naphthalene	None
5 Wt. Percent Gas -----	1.7	10-11
10 Wt. Percent IBP-430° F. Naphtha -----	8.2	10-15
Wt. Percent 430-925° F. Gas Oil -----	70.0	15-20
Wt. Percent Residue (Coke) -----	20.1	50-55

The above exemplary procedure illustrates the advantages of thermally depolymerizing higher molecular weight residua in the presence of a solvent with the exclusion of oxygen to convert the higher boiling materials to more valuable lower boiling gas oils.

Example 2

A 650° F.+ residua crude fraction (Bachaquero crude) was mixed at <150° F. with a >1:1 volume ratio of paraffinic C₃ to C₇ naphtha (naphtha to crude) while excluding oxygen, and allowed to settle for 0.5 to 6 hours. The insoluble residue was then filtered, and used as feed for the thermal depolymerization below. This feed material is solid at 100° F. and nonvolatile at vacuum distillation conditions corresponding to a nominal boiling point of 1000° F.+.

The conversion of these high molecular weight asphaltenes from Bachaquero crude obtained by naphtha solvent precipitation of virgin feed to useful oil products with less coke formation than encountered in conventional thermal treatment is demonstrated in a set of runs which also show the necessity of precluding contact with air. An added feature is the maintenance of low temperatures when the high boiling component (asphaltene) is in absence of the solvent. In this series of operations a charge consisting of 300 grams of asphaltene from Bachaquero crude and 300 grams of methyl naphthalene, together with 25 cc. of ammonium hydroxide as a polymerization inhibitor were charged to a one-liter stirred autoclave and were heated for 3 hours at autogenic (autogenous) pressure.

The product was discharged and recycle material was obtained by pentane precipitation, filtration, solvent extraction of the precipitate (leaving nonsoluble residue on the filter), and recovery of the solvent.

In the first two cycles benzene was employed as the extractant, and prior to the extraction the precipitated, unreacted asphaltene was air dried. Upon use of recycle methyl naphthalene, which was freed of peroxides by the recovery, the losses as insoluble residue were greatly reduced. This is shown by the following data.

50 THERMAL DEPOLYMERIZATION OF ASPHALTENES FROM BACHAQUERO CRUDE
[750° F., 3 hrs. on heat, 25 cc. NH₄OH solution in each cycle]

Cycle-----	1	2	3	4	5
Charge, Grams:					
Asphaltenes-----	300	167.5	100	150	150
Methyl Naphthalene-----	300	300.5	300	240	2450
Recycle Product-----		132.5	200	220	
Method of Recovery from Precipitated Autoclave Prod.	Benzene Ext.		Methyl Naphthalene Ext.		
			Soxhlet	Solution	Reflux
	Recovered Products, Grams:				
IBP-430 Naphtha-----	29.5	15.2	18.8	22	14.5
480+ Gas Oil-----	110	124	115	89	91
Residue-----	81	104		16	11.9
Wt. Percent Residue on Asphaltene Charge---	27	39		11	8

¹ Methyl naphthalene recovered in Cycle 3.

² About 250 grams recycle methyl naphthalene and 200 grams recycle product.

In the same series of operations attempts to extract the recycle product from the pentane precipitate with methyl naphthalene were unsuccessful until air was excluded and the extraction was conducted under a hydrogen blanket. This is shown by the following data.

THERMAL DEPOLYMERIZATION OF ASPHALTENES FROM BACHAQUERO CRUDE
[750° F., 3 hrs. on heat, 25 cc. NH₄OH soln. in each cycle]

Cycle.....	6	7	8	9	10	11
Charge, Grams:						
Asphaltenes.....	150	150	150	100	100	100
Methyl Naphthalene.....				250	65	300
Recycle Product.....	450	474.2	450	250	1,435	200
Method of Recovery from Precipitated Autoclave Prod.	Soxhlet Extraction ¹ without H ₂ Blanket			Soxhlet Extraction ² with H ₂ Blanket		
Recovered Products, Grams:						
IBP-430° F. Naphtha.....	19.5	12	13.5	38.5	7	15.5
450° F.+ Gas Oil.....	111	89	94	60	85	57
Residue.....	50.5	33	62	9	12	10
Wt. Percent Residue on Asphaltene Charge.....	34	22	41	9	12	10

¹ 235 grams of asphaltenes recovered from operation similar to Cycle 1.

² Extracted with methyl naphthalene at about 150-175° F. prior to Soxhlet extraction at about 450° F.; all operation under hydrogen blanket.

THERMAL DEPOLYMERIZATION OF ASPHALTENES, BACHAQUERO CRUDE
[3 hours residence time, 720-728° F., autogenous pressure]

	Feed Asphaltenes	Recovered Products		
		450° F.+ Gas Oil	Unreacted Asphaltenes	Residue
Grams.....	147	124	39.9	2.6
Conradson Carbon, Wt. Percent.....	45	8	66	¹ N.D.
Nickel, p.p.m.....	300	38	2,000	¹ N.D.
Vanadium, p.p.m.....	2,400	74	4,000	7,000

¹ N.D.=Not determined.

Example 3

The filtrate containing the n-pentane asphaltene precipitation solvent employed in Example 2 together with the oil product produced was fractionated in a laboratory column (15/5 distillation) to provide the naphtha yields, solvent for recycle, and the 480° F.+ gas oil fractions. The conversion to gas oil of low metals content and solids, leaving a material for further recycle, is demonstrated by the recovery from cycles 9-11. These results are:

A conversion of the Conradson carbon content of the asphaltenes to low Conradson carbon, low metals gas oil is demonstrated. The metals content of the feed is concentrated in the insoluble residue.

Example 5

The features of liquid phase thermal treatment in presence of a solvent essentially in the absence of oxygen, separation of the unreacted material from the lower boiling components, solution of the unreacted material in the

	Fresh Components		Recovered Products		
	Fresh Asphaltenes	Recycle Asphaltenes	480° F.+ Gas Oil	Recycle Asphaltenes	Residue
Grams.....	300	485	318	157	31
Conradson Carbon, Wt. Percent.....	45		4	61	¹ N.D.
Nickel, p.p.m.....	300		6	600	¹ N.D.
Vanadium, p.p.m.....	2,400		18	3,300	37,000

¹ N.D.=Not Determined.

Example 4

An operation similar to that of Example 2 was carried out except that no fresh asphaltenes were recharged and the solvent was reagent grade tetralin instead of methyl naphthalene. Starting with a charge of 147 grams of asphaltenes from Bachaquero crude in 394 grams of tetralin the depolymerization was conducted at 728° F. and the autoclave product pentane precipitated, filtered and the gas oil product was recovered from the filtrate. The precipitate was extracted with tetralin in the absence of air, i.e., with a hydrogen blanket, and the extract was removed for recycle leaving the residue on the extraction thimble. A total of four such cycles was made each with fresh tetralin following which the unreacted asphaltenes were recovered for inspection. Of the 147 grams

solvent, recovery of the insoluble residue by filtration was followed but with a different feed and a different technique. For this work the tetralin solvent was first freed of peroxides by refluxing in an atmosphere of hydrogen and the water was removed as vapor. The treated solvent was blended with West Texas vacuum bottoms in the weight ratio of 1530/1519. The one liter stirrer autoclave was charged with 504 grams of this mixture and after purging with nitrogen and then with hydrogen, the thermal depolymerization was conducted for 3 hours at 750° F. at autogenic pressure.

The products were flashed from the autoclave first at atmospheric pressure and then at about 0.5 mm. Hg and 450° F. The flashed products were set aside for later workup. The autoclave was recharged with the original

mixture of tetralin and the residuum bottoms and tetralin other than that in the blend to compensate for the material removed in the flashing operation and to maintain the same amount of tetralin originally present.

The thermal depolymerization was repeated through eleven such cycles. Thereupon, the nonvolatile material remaining in the autoclave was dissolved in tetralin and the solution was removed and filtered. The residue was further extracted with tetralin in Soxhlet equipment and then with benzene to remove the highly boiling solvent. The filtrate and tetralin Soxhlet extracts were combined and were vacuum distilled to yield the 1000° F.+ bottoms. The combined overheads from the flashing of autoclave products and vacuum distillation of the extracts were fractionated in a laboratory column into C₅-300° F. naphtha, 300-400° F. naphtha, 400-450° F. solvent fraction, and 450° F.+ gas oil. This operation is summarized as follows:

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THERMAL DEPOLYMERIZATION OF WEST TEXAS VACUUM RESIDUUM
[Tetralin solvent, eleven 3-hour cycles at 750° F.]

	Residuum Feed	Products				Residue
		C ₅ -300° F. Naphtha	300-400° F. Naphtha	450-1000° F. Gas Oil	1,000° F.+ Unreacted	
Grams.....	755	42	73.8	277	344	6.8
Gravity, ° API.....		47.3	23.0	24.8		
Conradson Carbon, Wt. Percent.....	16.5	0	0	0	19.6	
Nitrogen, Wt. Percent.....	0.4			0.13	0.6	
Sulfur, Wt. Percent.....	2.4			1.2	1.8	
Nickel, p.p.m.....	31			1	30	
Vanadium, p.p.m.....	27			1	25	
Vol. Percent above 650° F.....				40		

Worthy of note is (1) the conversion of Conradson carbon material in the residuum feed to gas oil, (2) the reduced sulfur content of the gas oil as compared to the feed, (3) the negligible metal content of the gas oil, (4) the boiling range of the gas oil with 60% in the 450-650° F. range, (5) the concentration of the metals components in the insoluble residue, and (6) the low amount of residue produced in this operation. The outstanding quality of the gas oil makes it an excellent feed for catalytic cracking and hydrocracking operations.

liter autoclave and air was expelled by purging with nitrogen and then with hydrogen. The system was pressurized with hydrogen at 500 p.s.i.g. at ambient temperature and was heated to 750° F. and the temperature was maintained at this level for one hour. Thereupon, the products were flashed first at atmospheric pressure which provided a cooling of the autoclave and then at about 0.5 mm. Hg pressure at a temperature of about 600° F.

Methyl naphthalene recovered from a similar operation and refluxed to remove peroxides which may have formed in the interim period was recharged to the autoclave to approximately the same methyl naphthalene content and the operation was repeated. A total of three such cycles were made employing only the original asphaltene charge and the internal recycle of the unreacted portion. The material remaining in the autoclave was suspended in methyl naphthalene and the blend of solution plus solids was filtered under a hydrogen blanket. The filter cake

was further extracted with methyl naphthalene and then with benzene to remove the high boiling solvent.

The filtrate and the methyl naphthalene extracts were vacuum distilled to yield the unreacted 1000° F.+ bottoms. The combined overhead products from the flashing operations and the vacuum distillation of the filtrate and extracts were fractionated in a laboratory column (15/5 operation) using 15 theoretical plates at a 5 to 1 reflux ratio, to yield the naphtha, the solvent and the 485° F.+ gas oil fraction. This is summarized as follows:

THERMAL DEPOLYMERIZATION OF ASPHALTENES FROM WEST TEXAS CRUDE-METHYL NAPHTHALENE SOLVENT
[One hour at about 700 p.s.i.g. H₂ partial pressure, 750° F.]
[Maximum total pressure during run=1600 p.s.i.g.]

	West Texas Asphaltene	Recovered Product		
		485-1,000° F. Gas Oil	Unreacted 1,000° F.+ Prod.	Solids Residue
Grams.....	277	99	183	0.9
Conradson Carbon, Wt., Percent.....	39.6	0	50.2	
Sulfur, Wt., Percent.....	5.14	1.9	4.94	
Nitrogen, Wt., Percent.....	0.792	0.26	1.13	
Nickel, p.p.m.....		1	453	
Vanadium, p.p.m.....	120	1	259	

Example 6

A depolymerization is conducted in a manner similar to the method of Example 5, but a different polymeric material (1000° F.+ product) and a different solvent are employed. For this work five-1000 gram batches of West Texas Atmospheric residuum were precipitated with normal pentane in a 5/1 volume ratio which yielded 357 grams of asphaltene. This product was vacuum dried and the dried product was maintained under a hydrogen blanket so as to avoid an oxygen uptake from the atmosphere. A solution of 277 grams of these asphaltene in 351 grams of methyl naphthalene was charged to the one-

As in Examples 2, 3, 4, and 5 the recovered gas oil is of much lower sulfur and metals content than the feed. Again the negligible amount of metals in the gas oil makes this product a very good feed for either catalytic cracking or hydrocracking.

What is claimed is:

1. A noncatalytic, liquid-phase process for converting heavy high boiling residua having a relatively high content of sulfur and metals to lower boiling gas oils having reduced sulfur and metals content consisting essentially of the steps of

(A) heating an intimate blend of said residua and 0.5:1 to 5:1 volumes of an aromatic solvent boiling in the

range of 150–800° F. at a temperature in the range of 650–900° F. and a residence time of 0.1 to 6 hours and

(B) separating a low sulfur, low metals gas oil fraction from the reaction mixture,
said steps (A) and (B) being carried out in an essentially oxygen-free atmosphere.

2. A process as in claim 1 where said residua has an initial boiling point of about 650° F.+ and a molecular weight ranging from 200 to 20,000.

3. A process as in claim 1 wherein said blend is prepared by heating said residua and said solvent at temperatures of 200 to 450° F.

4. Process according to claim 1 in which the oxygen free atmosphere is obtained by blanketing the process steps with an inert gas.

5. Process according to claim 4 in which the gas is hydrogen.

6. Process according to claim 1 in which the molecular oxygen content of the residua and solvent is less than 0.1 wt. percent based on the blend.

7. A noncatalytic, liquid phase process for converting asphaltenes to gas oil consisting essentially of the steps of
(A) separating the asphaltene fraction from heavy high boiling residua,

(B) heating an intimate blend of said asphaltenes and 0.5:1 to 5:1 volumes of an aromatic hydrocarbon solvent boiling in the range of 400–600° F. at a temperature in the range of 670–775° F. and a residence time of 1–4 hours,

(C) filtering solids from the reaction mixture and recovering a liquid reaction mixture, and

(D) fractionating the liquid reaction mixture to obtain a gasoline fraction, a solvent fraction, and a gas oil fraction having a boiling range of about 430–1000° F.,

said steps (A), (B), (C) and (D) being carried out in an essentially oxygen-free atmosphere.

8. A noncatalytic, liquid phase process for converting high boiling residua having a relatively high content of sulfur and metals to lower boiling gas oils having re-

duced sulfur and metals content consisting essentially of the steps of

(A) heating an intimate blend of said residua having an A.P.I. gravity of 0°–200°, a molecular weight of 400–600 and an initial boiling point above about 950° F. with 0.5:1 to 5:1 volumes of an aromatic solvent boiling in the range of 150–800° F. at a temperature in the range of 650–900° F. and a residence time of 0.1–6 hours,

(B) passing the reaction mixture to a primary separation zone,

(C) separating a fraction boiling above about 1000° F., said fraction containing unreacted material and sulfur and metal compounds,

(D) fractionating the fraction boiling below about 100° FF. to recover gasoline, solvent and gas oil,

(E) dissolving the fraction of Step (C) in the solvent, and

(F) recycling the solution of Step (E) to the heating Step (A),

Steps (A), (B), (C), (D), (E), and (F) being carried out in an essentially oxygen-free atmosphere.

9. Process according to claim 8 in which the separation in the primary separation zone consists of precipitation with a C₃+ paraffinic hydrocarbon solvent.

10. Process according to claim 8 in which the separation in the primary separation zone consists of vacuum flashing.

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