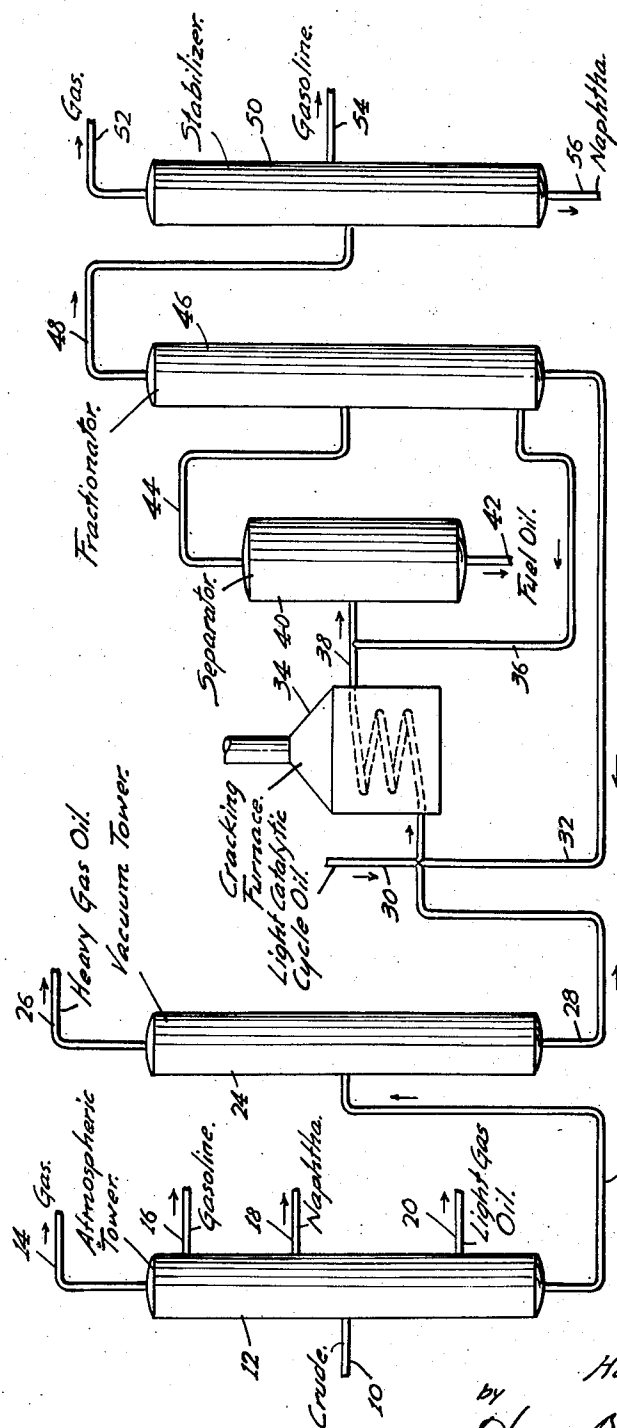


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VISBREAKING OF REDUCED CRUDE IN THE PRESENCE
OF LIGHT CATALYTIC CYCLE STOCK
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VISBREAKING OF REDUCED CRUDE IN THE PRESENCE OF LIGHT CATALYTIC CYCLE STOCK

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5 Claims. (Cl. 208—106)

This invention relates to a thermal conversion process for the thermal conversion of petroleum fractions, and more particularly to a process in which catalytic cycle stocks and very heavy petroleum residues are converted to more volatile and valuable products by thermal conversion.

In the processing of petroleum crude oils, the crude is ordinarily first passed through a distillation column at substantially atmospheric pressure in which gas and gasoline are removed as overhead products, naphtha and perhaps a light gas oil are taken off as side streams, and the heavier fractions are discharged as bottoms from the tower. The bottoms from the atmospheric tower are then passed through a vacuum distillation tower in which a heavy gas oil is taken overhead and a heavy residual fraction is obtained from the bottom of the vacuum tower. The large and steadily increasing demands for the more volatile petroleum products, notably gasoline and distillate fuel oils, and the necessity of processing heavier, less desirable crudes, has forced refiners to make deeper and deeper cuts into the crude.

Gas oils obtained as distillates from the atmospheric and vacuum distillation towers are generally cracked by either thermal or catalytic processes to form gasoline. In catalytic cracking processes, a very refractory cycle oil having a relatively high content of aromatics is produced along with the gasoline. Attempts to crack the cycle oils further, either catalytically or thermally, have generally been unsatisfactory. In catalytic processes, large amounts of carbon are deposited on the catalyst and low conversions to gasoline are obtained. In thermal processes, very severe cracking conditions, together with very high recycle ratios, are required to obtain a satisfactory conversion to gasoline. Often recycle ratios as high as 4 parts of recycle to 1 part of fresh feed are employed, with a consequent serious reduction in the capacity of the thermal cracking unit. Because of the difficulty in cracking the catalytic cycle oil further, that stock is largely used to cut the viscosity of heavy fuel oils to meet specifications and blended with virgin fuels to form furnace oil. Both of these uses of the catalytic cycle oil, and particularly its use to cut the viscosity of heavy fuel oils, seriously decrease the return from the catalytic cycle oil as compared with what might be obtained if the catalytic cycle oil could satisfactorily be converted to gasoline.

Residual stocks from atmospheric distillation towers have customarily been subjected to a vis-breaking thermal cracking operation which is essentially a mild cracking operation at temperatures usually in the range of 825° F. to 900° F. More severe cracking conditions are not possible because of excessive coke formation. Recently, it has been found that, contrary to expectations, residual stocks much heavier than those from atmospheric distillation towers, may be vis-broken under more severe conditions, such as temperatures of approximately 900° F. to 950° F., without excessive coke formation. That discovery is the subject matter of Application Serial No. 262,566 now U.S. Patent No. 2,762,754 of William C. Offutt,

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Paul Siecke, and Harold Beuther, filed December 20, 1951.

This invention provides a process in which a better distribution of the products obtained from petroleum crudes is obtained and particularly one in which the yield of gasoline is increased. According to this invention, a light catalytic cycle oil is mixed with a very heavy residue from crude petroleum which has been deeply reduced by vacuum distillation, and the mixture is heated and thermally cracked in furnace coils at severe cracking conditions comparable to those used for vis-breaking the very deeply reduced residues from vacuum stills mentioned above. The yield of gasoline from the heating and cracking of the mixture is markedly increased over that obtained when, for example, the catalytic cycle oil and the residue are separately cracked under comparable conditions. Moreover, the mixture may be cracked at even more severe conditions than the very heavy residue alone without excessive coke formation.

The single figure of the drawings is a diagrammatic representation of a flow sheet of the process of this invention. Valves, meters, pumps, condensers, reflux lines and other control equipment have been omitted from the drawing for simplification.

Referring to the drawings, the feed stock, which ordinarily will be a whole petroleum crude oil but may be a partially reduced crude, is introduced through a line 10 into an atmospheric distillation tower 12 from which gas is taken off overhead through line 14, and side streams of gasoline, naphtha and light gas oil may be withdrawn through side tower outlets 16, 18 and 20, respectively. The bottoms from the atmospheric tower 12 are withdrawn through line 22 and passed into a vacuum distillation tower 24 in which a very deep cut is made to produce an exceptionally heavy petroleum residue as bottoms. A heavy gas oil is withdrawn at the top of the tower 24 through line 26 and passed to apparatus, not shown, for further processing, such as by catalytic cracking. A very heavy residual fraction is withdrawn from the bottom of tower 24 through line 28. It will be appreciated that the atmospheric tower 12 and vacuum tower 24 are provided with the usual reflux equipment and other apparatus necessary for control of the operation of the towers. If necessary, a heater (not shown) may be used between the atmospheric and vacuum tower to supply the heat necessary for the deep vacuum reduction of the bottoms from the atmospheric tower 12.

The extent of the reduction of the crude required to produce a charge stock suitable for use in the process of this invention will depend in part upon the nature of the crude. In some instances, for example, where the crude is of a paraffin base, the residue withdrawn through line 28 may be only approximately 5% of the crude. With other crudes, such as a West Texas crude, the residue withdrawn from the bottom of the distillation tower 24 may constitute approximately 10% of the crude. In general the heavier the crude, the larger the percent of the total crude that may be treated satisfactorily according to this invention. Residues from certain heavy crudes such as those from Kuwait and Mississippi may constitute as much as 20% and 30% of the crude, respectively. It has been found that the residual fractions which may be successfully cracked according to this invention are those having a carbon residue number of at least 18, a gravity in ° A.P.I. below 10 and an SUS viscosity at 210° F. of at least 6,000. The initial boiling point of the residual fractions will generally be from 900° to 950° F., but will depend in part on the fractionating efficiency of the vacuum tower 24.

According to this invention, the residue from the bottom of tower 24 is mixed with a light catalytic cycle oil introduced into line 28 through a line 30. The light

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catalytic cycle oil may be obtained from any of the well-known catalytic cracking processes such as the Houdry fixed bed process, moving bed processes, or fluid catalytic cracking processes. The boiling range of the light catalytic cycle stock will ordinarily be within the range of 400° F. to 650° F., and preferably within the range of 400° to 600° F. It will be appreciated that any suitable method of mixing the two fractions may be employed, and that a mixture of the residue with the light catalytic cycle oil may be stored in suitable tanks and charged directly to the furnace, rather than mixing the two fractions in the line 28. The ratio of catalytic cycle oil to the residue may range from approximately 2 to 1, to 1 to 6.

Preferably, in the operation of the process of this invention, it will be desirable to recycle fractions of the cracked product boiling above the gasoline range, as illustrated in the drawings. The recycle oil is introduced into line 28 from line 32 for admixture with the light catalytic cycle oil and the residue prior to heating in the furnace 34.

The mixing of the light catalytic cycle oil with the residue from the vacuum tower 24 permits the use of more severe cracking conditions in the furnace 34 than is possible in the usual visbreaking operation without the formation of the excessive coke which limits the cracking conditions in conventional visbreaking processes. For example, the short time conversion process of this invention will ordinarily be accomplished with a furnace outlet temperature in the range of about 900° F. to 1000° F., and preferably from approximately 950° F. to 1000° F. The upper temperature limit will be determined in part by the heating curve of the furnace. If extremely high heating rates are possible, temperatures above 1000° F. may be used, in some instances, without excessive coke formation. The pressure is not as important as the temperature in controlling the reaction rate and severity of cracking. A pressure in the range of 50 to 1000 p.s.i. gauge will ordinarily be used. The coil volume above 750° F. will be from about 0.020 to 0.035 cubic feet per barrel per day. In the preferred form of the invention illustrated in the flow sheet, the mixture of the light catalytic cycle oil, recycle oil, and the residue is quenched immediately after its discharge from the furnace outlet by means of a stream of quenching oil introduced through line 36.

The cracked products from the furnace 32 are discharged through line 38 into a separator 40 from which heavy fuel oil is withdrawn as a bottoms product through a line 42 and the more volatile products are withdrawn overhead through a line 44. The conditions in the separator are controlled to regulate the initial point of the fuel oil. In this manner, the end point of the recycle oil is also regulated, ordinarily to form a recycle oil having a boiling range of approximately 400° to 600° F.

The overhead product from the separator 40 is delivered through a line 44 into a fractionating tower 46 which separates the more volatile compounds from the 400° to 600° recycle oil withdrawn from tower 46 through line 32 for recycling through the furnace 34. The overhead products from tower 46 are delivered through a line 48 into a stabilizer 50 from which gases are withdrawn as an overhead product through line 52. Gasoline is taken from stabilizer 50 as a side product through line 54, and 400° F. end point naphtha is withdrawn as bottoms through line 56. The fractionator and stabilizer illustrated are conventional and shown only to complete the disclosure. Clearly, other fractionating and stabilization apparatus and procedures may be employed without departing from this invention.

It has been found that the process of this invention gives an improved yield of gasoline particularly as compared with processes in which the light catalytic cycle oil and heavy reduced crude are separately cracked. In addition, there is apparently less condensation to form

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heavy, tar-like compounds, thereby reducing the cutter oil requirements for the preparation of fuel oil of acceptable viscosity, and the consequent degradation of the cycle stock to products of lower value.

The light catalytic cycle oils are relatively high in aromatic content. Without wishing to be bound by any theory concerning the mechanism of this invention, it is believed that the solvent nature of the light catalytic cycle oil dissolves very heavy condensation or polymerization products formed during cracking. Moreover, the gas oil markedly increases the volume of vapor formed in the tubes of the furnace and, as a result, increases the velocity in the tubes to sweep any coke which may be formed from the coils.

The following examples illustrate the improved operations made possible by this invention:

EXAMPLE 1

A West Texas crude oil was reduced in an atmospheric and vacuum distillation process of the type described to form a residual product constituting 9.9% of the crude. A light catalytic cycle stock boiling in the range of approximately 436° F. to 616° F. was added to the residue, in such proportions that the reduced crude constituted 72% of the mixture and the catalytic cycle stock the remainder, to form a total charge. The charge was cracked in a coil at a maximum temperature of 950° F. and a pressure of 400 p.s.i.g. in a short period cracking operation. The cracked products were fractionated to produce a 10 lb. Reid vapor pressure, 400° F. end point gasoline and a specification fuel oil. The fraction boiling between the end point of the gasoline and the initial boiling point of the specification fuel oil was recycled to extinction. The recycle oil amounted to 112% of the total charge.

EXAMPLE 2

The residue constituting 9.9% of a West Texas crude employed in Example 1 was cracked in a single pass conversion without the addition of catalytic cycle stock. The single pass conversion was conducted in a coil at a maximum temperature of 950° F., and pressure of 200 p.s.i.g., and the cracked products were fractionated to produce a 10 lb. Reid vapor pressure, 400° F. end point, gasoline, and a specification fuel oil, as in Example 1.

EXAMPLE 3

A residue from vacuum distillation constituting 17.7% of Kuwait crude was mixed with a light catalytic cycle stock similar to that employed in Example 1 in proportions of 68% reduced crude and 32% catalytic cycle stock to form a total charge. The charge was cracked at a maximum temperature of 950° F. and a coil outlet pressure of 400 p.s.i. gauge. The cracked products were separated into 10 lb. Reid vapor pressure, 400° F. end point, gasoline, and specification fuel oil. The fraction boiling between the end point of the 400° F. gasoline and the initial boiling point of the specification fuel oil was recycled to extinction. The recycle oil amounted to 111% of the total charge.

EXAMPLE 4

A residue constituting 17.7% of a Kuwait crude was cracked in a single pass operation without the addition of catalytic cycle stock. The maximum temperature of the cracking operation was 955° F., and a pressure of 200 p.s.i.g. was employed.

In each of Examples 1 through 4, the time of cracking was substantially the same, as indicated by the coil volume above 750° F. of approximately 0.02 cubic feet per barrel of throughput per day. The results of the opera-

tions in Examples 1 through 4 are illustrated in the following Table I:

Table I

	Exam- ple 1	Exam- ple 2	Exam- ple 3	Exam- ple 4
Yield of 10 RVP 400° F. E.P. gasoline:				
Percent by vol. of total charge...	27.8	12.4	32.5	18.4
Yields: Percent by vol. of crude—				
10 RVP 400° F. E.P. gasoline....	3.8	1.2	8.4	3.3
Fuel oil.....	10.8	11.5	18.7	20.2
Catalytic cycle stock requirement.....	4.7	2.7	9.8	5.4
Charge.....	3.8	0.0	8.5	0.0
Cutting oil.....	0.9	2.7	1.3	5.4

If the light catalytic cycle stock added to the residue in Examples 1 and 3 is cracked separately to extinction in a recycle operation at conditions corresponding to the severity of Examples 1 and 3, and the resultant products combined with the products from Examples 2 and 4, the yields of gasoline and fuel oil obtained by cracking the fractions separately are obtained. A comparison of the yields of gasoline and fuel oil obtained by processing of the combined heavy residues and light catalytic cycle stock according to this invention with yields obtained by processing of the stock separately is set forth in Table II. The separate cracking of cycle stock and the residue of Example 2 is reported as Example 5 and of cycle stock and the residue of Example 4, as Example 6.

Table II

	Exam- ple 1	Exam- ple 5	Exam- ple 3	Exam- ple 6
Yields: Percent by Vol. of Total Charge—				
10 RVP 400° F. E.P. Gasoline....	27.8	20.4	32.5	25.3
Fuel Oil.....	78.3	81.2	71.4	72.9

It will be noted that a substantial increase in the yield of gasoline is made possible by this invention. Additionally, the amount of fuel oil obtained from the crude is reduced by almost 10%, and the amount of catalytic cycle stock required to cut the fuel oil to the viscosity necessary to meet specifications is markedly reduced.

The following example shows the results of cracking a deeply reduced West Texas crude, similar to that of Example 1 at more severe conditions:

EXAMPLE 5

A West Texas crude was reduced by successive atmospheric and vacuum distillation steps to form a residue constituting 9.9% of the original crude. A total charge was prepared by blending the residue with a light catalytic cycle stock having a boiling range of approximately 400° F. to 600° F. in proportions of 3 parts by volume of residue to 1 part by volume of cycle stock. The total charge was mixed with recycle oil and cracked in a furnace coil at a maximum temperature of 965° F. and a pressure of 400 p.s.i.g. The recycle oil consisted of the fraction of cracked products boiling between the end point of the gasoline (400° F.) and the initial boiling point of the specification fuel oil. The recycle oil amounted to approximately 128% of the volume of the total charge. The results of the conversion are illustrated in Table III:

Table III

Residue feed	9.9% by vol. West Texas.
Flow rate, percent of total charge:	
Residue	75 percent.
Light catalytic cycle stock ..	25 percent.
Recycle oil	128 percent.
Furnace outlet, temperature	965° F.
Furnace pressure	400 p.s.i.g.

Furnace coil volume above 750° F. 0.02 cu. ft./bbl. of throughput/day.

Yields, vol. percent of total oil charge—

5	Gas, C ₃ and lighter	3.4.
	Butane-butene	2.9.
	Debutanized 400° F. E.P. gasoline	27.0.
10	Yield of 10 lb. R.V.P. stabilized gasoline vol. percent of total charge	29.6.
	Fuel oil yield, vol. percent of total crude	11.3.
15	Cutting oil, vol. percent of total crude	2.0.
	Total light catalytic cycle stock, vol. percent of total crude	5.2.

I claim:

20 1. A process for the thermal conversion of petroleum hydrocarbons comprising vacuum distilling a petroleum oil to form a heavy residue as a bottoms product having a gravity in °API of less than 10, Conradson carbon residue number of at least 18, and an SUS viscosity at 210° F. of at least 6000, mixing the residue with a light catalytic cycle oil having a boiling range of approximately 400–650° F. to form a mixture having a ratio of residue to light catalytic cycle oil ranging from 1:2 to 6:1, heating the mixture to a temperature of 900 to 1000° F. in a short period to crack residue and light catalytic cycle oil in the mixture, separating the cracked products into fuel oil and a vapor phase, fractionating the vapor phase to produce gasoline and a recycle oil having a higher boiling range than gasoline as separate fractions, and returning recycle oil to the mixture for heating to cracking temperatures.

2. A process for the thermal conversion of a heavy residue from the vacuum distillation of a petroleum oil, said residue having a gravity in °API of less than 10, a Conradson carbon residue number of at least 18 and an SUS viscosity at 210° F. of at least 6,000, comprising mixing the residue with a light catalytic cycle oil boiling in the range of approximately 400–650° F. to form a mixture having a ratio of residue to light catalytic cycle oil ranging from 1:2 to 6:1, rapidly heating the mixture to a temperature of 950–1000° F. in a coil having a volume above 750° F. less than about 0.035 cubic feet per barrel of throughput per day to crack the mixture, the time at the high temperature causing cracking of hydrocarbons of both the residue and light catalytic cycle oil, separating the cracked products into a liquid phase and a vapor phase, fractionating the vapor phase to produce gasoline and a recycle oil having a higher boiling range than gasoline as separate fractions, and returning recycle oil to the mixture for heating to cracking temperatures.

3. A process for the thermal conversion of a heavy residue from the vacuum distillation of a petroleum oil, said residue having a graviting in °API of less than 10, a Conradson carbon residue number of at least 18, and an SUS viscosity at 210° F. of at least 6,000, comprising mixing the residue with a light catalytic cycle oil having a boiling range of approximately 400–650° F., in a ratio of residue to light catalytic cycle oil range from 1:2 to 6:1, rapidly heating the resulting mixture to a temperature of 950–1000° F. in a coil having a volume above 750° F. not exceeding 0.035 cubic feet per barrel of throughput per day to crack residue and light catalytic cycle oil in the mixture, quenching the heated mixture, separating the cracked products into a fuel oil and a vapor phase, and fractionating the vapor phase to separate a gasoline fraction.

4. A process for the thermal conversion of petroleum hydrocarbons comprising vacuum distilling a crude oil to form a heavy residue as a bottoms product having a gravity in °API less than 10, a Conradson carbon residue

number of at least 18, and a SUS viscosity at 210° F. of at least 6,000, mixing the residue with a light catalytic cycle oil boiling in the range of approximately 400–650° F. to form a mixture having a ratio of residue to light catalytic cycle oil ranging from about 1:2 to 6:1, heating the mixture to a temperature of 900–1000° F. to crack residue and light catalytic cycle oil in the mixture, and separating the cracked products into a cracked residual oil and cracked distillate fractions.

5 10 15 5. A process for the thermal conversion of petroleum hydrocarbons comprising vacuum distilling a petroleum oil to form a heavy residue having a gravity of degrees API less than 10, a Conradson carbon residue number of at least 18, and a SUS viscosity at 210° F. of at least 6,000, mixing the residue with a light catalytic cycle oil boiling in the range of approximately 400 to 650° F. to form a mixture having a ratio of residue to light catalytic

cycle oil ranging from about 1:2 to 6:1, heating the mixture to a temperature of 950 to 1000° F. to crack residue and light catalytic cycle oil in the mixture, and separating the cracked products into a cracked residual oil and cracked distillate fractions.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,900,327

August 18, 1959

Harold Beuther

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 6, line 58, for "graviting" read -- gravity --; column 7, line 12, for "gravity of" read -- gravity in --.

Signed and sealed this 1st day of March 1960.

(SEAL)

Attest:

KARL H. AXLINE

Attesting Officer

ROBERT C. WATSON
Commissioner of Patents