Sept. 13, 1960 E. L. CLARIDGE 2,952,613

PROCESSING PETROLEUM OILS

Filed March 13, 1956 2 Sheets-Sheet 1

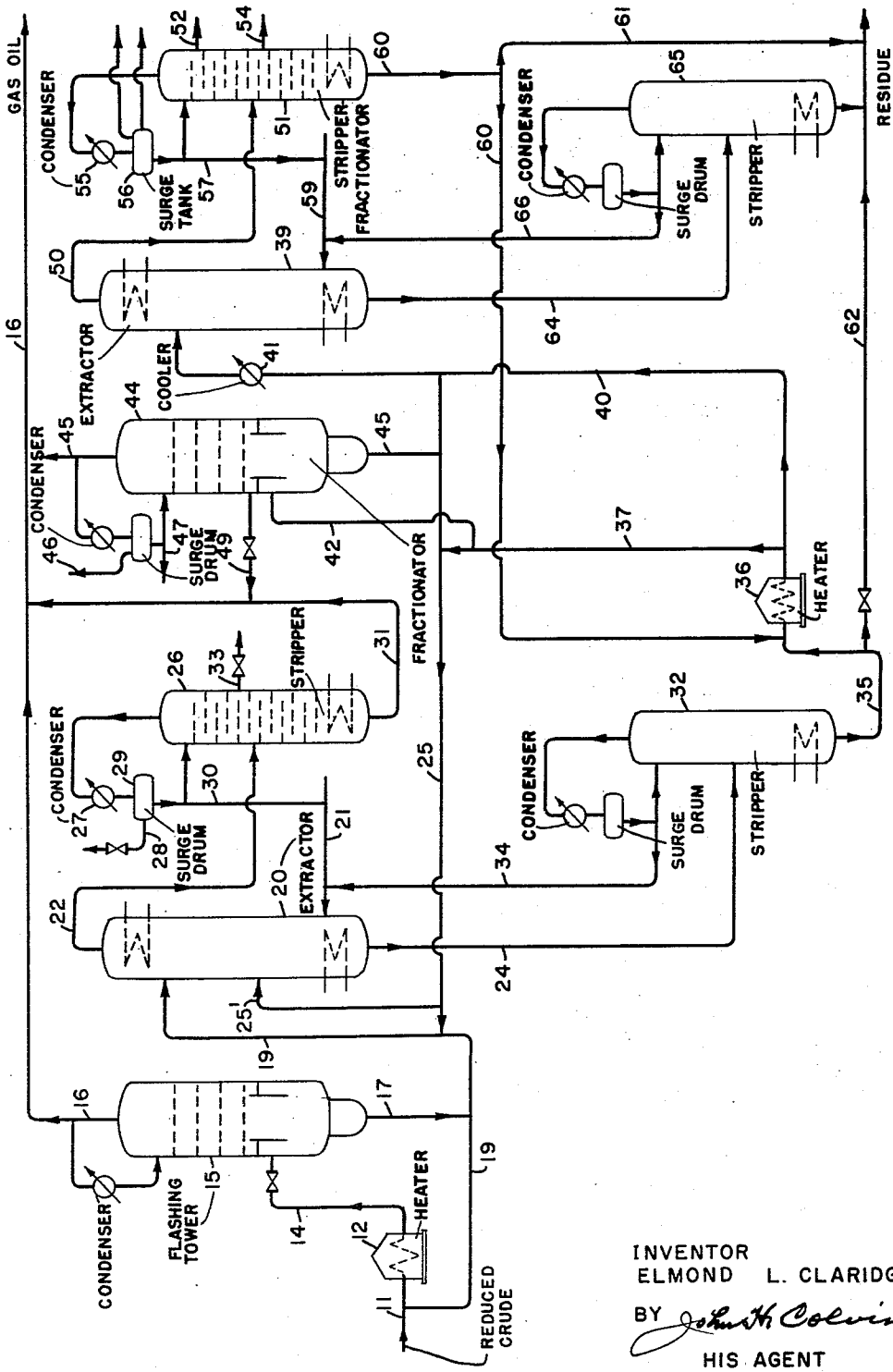


FIG. I

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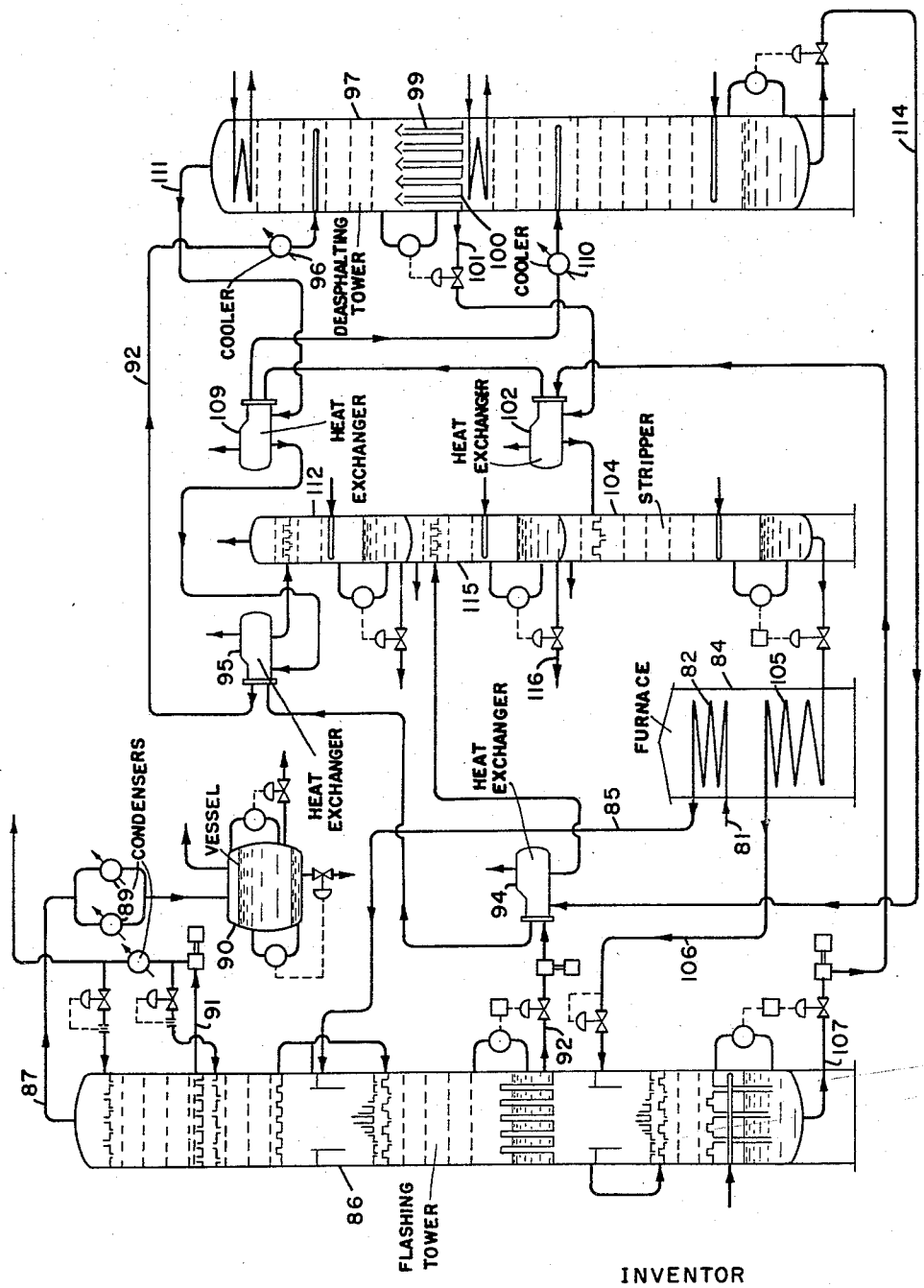


FIG. II

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2,952,613

PROCESSING PETROLEUM OILS

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Filed Mar. 13, 1956, Ser. No. 571,168
9 Claims. (Cl. 208—73)

This invention relates to a petroleum refining process. More particularly, it relates to an improved process for the preparation of catalytic cracking feed stock from petroleum oils which contain asphaltic constituents, such as crude petroleum, partially reduced crude oil, or the like.

Various methods have been proposed and utilized for the recovery of clean oils and fractions thereof from crude oil, topped crude oil, reduced crude, and the like. Thus, atmospheric and vacuum distillations, as well as steam distillation, without cracking and sometimes with mild thermal cracking, as in visbreaking, are well known commercial methods for the production of various distillates, such as gasoline, kerosene, light gas oil, heavy gas oil and distillate lubricating oils. On the other hand, the asphaltic and resinous bodies present in varying amounts in different crude oils have been separated by precipitation from the oil with light hydrocarbons, such as in propane deasphalting operations, to yield a deasphalted oil, which, in many cases, is more or less equivalent to distillate fractions, such as a vacuum flashed distillate, as catalytic cracking feed material. However, the previously available methods, particularly when applied to oils which contain appreciable amounts of asphaltic material and metal contaminants, have suffered from the defect of not providing maximum yields of catalytic cracking feed stock while at the same time maintaining the oil at a high quality level for its use in the catalytic cracking operation. Consequently, it has been necessary to process more crude oil to provide the necessary amount of catalytic cracker feed stock of suitable high quality, or it has been necessary to reduce the oil throughput of the catalytic cracking unit because of the reduced activity of the catalyst caused by the poorer quality of the cracking feed stock and the concomitant increase in coke make in the reaction zone with resulting greater demand in the regeneration zone for burning off the coke on the catalyst.

It is a principal object of the present invention to provide an improved process for the production of catalytic cracking feed stock in enhanced yield and of improved quality from a crude oil which contains asphaltic constituents. A more specific object is to recover catalytic cracking feed, from straight run residue or vacuum flasher pitch, at higher yields and of better quality. It is a further object to provide a process for the production of higher yields of catalytic cracking feed from asphaltic residues, while at the same time producing an asphalt of good quality. These objects will be more fully understood and others will become apparent from the description of the invention, which is made with reference to the accompanying drawing, wherein:

Fig. I is a process design representing a suitable plant scheme for the practice of the invention; and

Fig. II is a diagrammatic sketch of another process design for the production of catalytic cracking feed stock from a reduced crude.

It has now been discovered that an increased yield of high quality cracking feed can be obtained from reduced crude oil containing asphaltic, resinous and metal-containing contaminant constituents, by a coordinated combination of operations wherein: (1) reduced crude is

treated with a deasphalting solvent under conditions controlled to separate only a portion of the oil components and only a minor proportion of the metal-containing contaminants in a separate oil-solvent phase from the asphaltic constituents; (2) the oily asphaltic residue is then mildly thermally treated to crack only a minor proportion of the oil components while converting metal-containing constituents to less volatile and less oil-soluble constituents and cracking some of the asphaltic (aromatic) components to produce paraffinic oil components; and (3) recovering a further amount of oil components from the asphaltic residue by extraction with a low molecular weight hydrocarbon.

In accordance with a more particular and preferred embodiment of the invention, the process comprises: (1) removing a substantial portion of the distillable catalytic cracking feed oil components from the reduced crude by vaporization at a low subatmospheric pressure, such as by a vacuum flashing, while avoiding thermal cracking; (2) extracting the residue from this partial vaporization separation with a light hydrocarbon deasphalting solvent and recovering a predominantly propane-soluble catalytic craking feed oil from the solvent extract; (3) thermally cracking the asphaltic residue from the extraction, thereby converting metal-containing components to less oil-soluble metal-containing substances and cracking asphaltic components to produce paraffinic oil components; (4) extracting the cracked product with a light hydrocarbon deasphalting solvent to recover a further amount of propane-soluble components; and (5) recovering predominantly propane-soluble catalytic cracking feed oil components from the resulting solvent extract. A still further preferred practice of the invention comprises recycling to the thermal cracking step (3) immediately above at least a portion of a propane-insoluble fraction which is separated from propane-soluble components in solvent extraction and recovery steps (4) and (5).

Thus, the process comprises at least two solvent deasphalting operations on the heavier asphaltic residual material with an intervening mild thermal cracking of at least once-deasphaltized material. The two deasphalting operations on the heavier fraction of material can be carried out in separate deasphalting zones, or in the same zone at separate times, or in the same zone at the same time.

The first solvent deasphalting operation is carried out under conditions of temperature, pressure, solvent-to-oil ratio, and the like, as will be well understood by those familiar with solvent deasphalting of asphaltic oils, to effect a separation of only a portion of the oil, such that the metal contaminants content thereof is maintained at a suitably low value. In general, the more paraffinic oil components will be extracted while a substantial proportion of the more aromatic and higher boiling oil components will remain with the asphaltic residue. The extent of the extraction in general will be limited at this stage to that which is extractable with propane alone, although it is not required that the solvent be propane alone. Not only do the oil components thus recovered, having for the most part molecular weights up to about 500, have superior catalytic cracking properties, but the low concentration of metal-containing contaminants minimizes the poisoning effect thereof on the catalyst, as well as the tendency to increase coke formation during the catalytic cracking.

The mild thermal cracking of the partially de-oiled asphaltic residual material serves the multiple purpose of: (*a*) converting high molecular weight oil components to lower molecular weight oil components of improved catalytic cracking characteristics; (*b*) producing suitable catalytic cracking oil feed components by cracking higher alkyl substituents from polynuclear asphaltic or resinous

substances while at the same time producing a molecular residue of reduced solubility in deasphalting solvent thereby providing for a sharper separation between asphaltic, coke-forming materials and quality oil components for catalytic cracking; and (c) converting the more oil-soluble organo-metal constituents to less oil-soluble metal-containing constituents so that they are more readily and effectively separated from the oil components by solvent deasphalting. The oil components in the oily asphalt feed to the mild thermal cracking also serve a diluent purpose in minimizing extensive condensation of dealkylated asphaltic type molecular residues to coke or coke-like bodies.

The exact set of conditions which is optimum for the mild thermal cracking depends on a number of factors, such as the nature of the heavy oil stock and other correlative conditions in the combination of operations. In general, the temperature suitably ranges from about 400° C. to about 500° C., the residence time from a few seconds to about 60 minutes, and the pressure from substantially atmospheric to a substantially superatmospheric pressure, which can be as high as 300–500 p.s.i.g. or even higher, although a pressure of from about 1 atmosphere to about 200 p.s.i.g. is preferable. It will understood that the higher temperatures are used at the shorter residence times, and vice versa. The conditions will usually be selected to limit the cracking of the material to gas and gasoline components to not over about 10% by weight, based on the material subjected to the thermal cracking, and suitably not over about 5%.

The lighter cracked products, such as the gas and gasoline components, and usually the lighter gas oil fraction, particularly those components lighter than the lightest oil in the feed to the first deasphalting operation, may be advantageously removed by distillation and/or flashing prior to subjecting the material to the subsequent deasphalting operation for the recovery of a further amount of catalytic cracking feed oil.

When the second deasphalting step is carried out separately from the first one, a deeper extraction of oil can be made without adversely affecting the quality of the recovered oil. As already pointed out, the thermal cracking has the effect of reducing the solubility of both the coke-forming asphaltic and resinous components and of the metal-containing components, so that more complete solution of the oil components in the solvent can be effected without dissolving an undesirable proportion of the deleterious materials.

In accordance with a further aspect of the invention, at least a portion of the heavier or less propane-soluble oil components of the thermally cracked product is subjected to a still further mild thermal cracking, preferably by recycling it to the previous cracking zone in admixture with other uncracked material. This is readily accomplished when the later deasphalting operation is accomplished in the first deasphalting zone simultaneously with the first deasphalting step. In that case, a portion of the asphaltic residue, comprising a blend of cracked and uncracked asphaltic components is suitably withdrawn as an asphalt product, if desired or necessary, in order to prevent too much build-up of higher melting asphaltenes in the recycling stream. When the two deasphalting operations are separate, the heavier or more aromatic portion of the deasphalted oil from the later deasphalting can be advantageously recycled to the thermal cracking zone, or it, with or without other oil components, can be recycled to the previous deasphalting step. When recycling the heavier components of the oil to the thermal cracking zone, the second deasphalting operation, when carried out separately, can be carried out to the extent of deliberately including some of the more oil-soluble metal-containing materials and asphaltic bodies in the extract, since they will be converted to separable components by the subsequent thermal treatment thereof.

Having described the general nature of the invention and various features thereof, its practice will be more readily understood from more detailed description of particular embodiments of it.

Referring specifically to Fig. I, a reduced crude, such as the bottoms from a Los Angeles Basin crude which has been distilled to remove the usual gas, light naphtha, heavy naphtha and gas oil fractions, as feed in line **11** is heated to flashing temperature by passage through a suitable furnace **12**, such as a coil or tube heater, and delivered by line **14** to a suitable flashing tower **15** provided with suitable vapor-liquid separating means, such as bubble-cap trays, grid trays, or the like, from which a portion of the distillable oil components is removed as an overhead flasher distillate in line **16** while the remainder is removed as a bottoms flasher pitch in line **17**. Although it is desirable to recover the maximum of distillate oil in this operation, a substantial proportion of distillable oil is invariably left in the pitch in commercial operations.

Although it is advantageous with many crude oil stocks to remove a portion of the heavier distillable oils, as by vacuum flashing, in order to make the subsequent extraction with a light hydrocarbon more effective, it is not necessary to do so in all cases. Hence, as indicated, the flasher pitch in line **17** may be utilized alone or admixed with a portion of reduced crude in line **19**, or the vacuum flashing operation may be by-passed entirely. The flasher pitch and/or reduced crude in line **19** is delivered to a suitable solvent extraction zone, as in extractor **20** wherein it is intimately contacted, as by countercurrent flow, with a suitable selective solvent for the oil but a non-solvent for asphaltic material, as well-known in the art, such as the lower molecular weight hydrocarbons. Propane or butane and mixtures thereof are well suited to the purpose. The details of temperature, pressure, solvent-to-oil ratios, and the like, of such so-called deasphalting operations are well understood in the art. By the use of propane or propane-butane mixture, a substantial portion of the oil content is readily recovered while leaving a substantial portion in the residue. The extraction conditions are selected so that the recovered oil, for the principal part, is made up of substances of molecular weights below about 500. By thus controlling the separation, the total metals content of the oil is kept below about 90 parts per million as metal.

The C_3/C_4 solvent, introduced by line **21**, is removed for the most part with oil in line **22**, the remainder being removed in line **24** with the remaining partially deoiled asphaltic residue. The reduced crude and/or flasher pitch may be suitably extracted in extractor **20** in admixture with thermally cracked asphaltic residual material, as produced at a later stage in the operation, delivered by line **25** to line **19** and/or line **25'**.

The solvent-oil extract in line **22** is then stripped in stripper **26** to recover the solvent as an overhead product which is suitably condensed in condenser **27** and collected in surge drum **29**, from which a portion is returned to the stripper to provide reflux and the remainder is recycled by lines **30** and **21** to the extractor **20**. Any lighter gases are readily removed by line **28** while lighter oils (naphtha), which will be present if the total subsequently cracked product stream is recycled to extractor **20**, may be readily withdrawn as one or more sidestreams as by line **33**. The stripped oil is withdrawn through line **31** and may be combined in line **16** with oil from the vacuum flasher to provide an enhanced yield of high quality catalytic cracking feed stock.

The propone-butane in the partially deoiled asphaltic residue in line **24** is stripped therefrom in stripper **32** and returned by lines **34** and **21** to the extractor. The stripped residue is withdrawn in line **35** and heated in heater **36** to effect a minor amount of thermal cracking equivalent to the production of from about 10% to about 30% by weight of material boiling up to about 400° F., based on the feed to the heater (cracker). The thermally cracked residue is then further extracted by light

hydrocarbon, as by recycling it by lines **37**, **25** and **19** to extractor **20**, or it can be extracted in a separate extractor **39**, to which all of it is delivered directly through line **40** and cooler **41**. On the other hand, the cracked product stream from heater **36** can be delivered by lines **37** and **42** to a suitable fractionator **44**, wherein lighter cracked products are separated as one or more distillate fractions, withdrawn by lines **45**, **46**, **47** and **49**, as desired, and the topped oily asphaltic residue withdrawn through line **45** and delivered either by line **25** to extractor **20** or by line **40** to extractor **39**. When it is further extracted in extractor **20**, a portion of the partially deoiled residue from stripper **32** will be withdrawn via line **62** to provide for constant removal of ultimate residue from the system.

Extraction of the cracked residue in extractor **39** may be carried out with a further portion of the same hydrocarbon or hydrocarbon mixture used in the first stage extraction in extractor **20**. However, a more complete recovery of the oil as well as of oil precursors is more readily secured by the use of a higher boiling hydrocarbon or mixture thereof, such as pentanes or hexanes, or a mixture of C_3–C_7 hydrocarbons having an average molecular weight of about that of the pentanes.

The extract removed overhead by line **50** is stripped of solvent, and of any lighter hydrocarbons, in stripper-fractionator **51**, any naphthas suitably withdrawn as one or more sidestreams, as indicated by lines **52** and **54**, and the heaviest portion of the oil, containing coke-forming and metal-containing components, withdrawn as a bottoms fraction. Recovered solvent is recycled to the extractor through condenser **55**, surge tank **56** and lines **57** and **59**. The bottoms fraction in line **60** from **51** may be subjected to a further thermal cracking, as by recycling it to heater **36**, to condition it for recovery of a further amount of suitable oil from it. However, a portion or all of it may be delivered by line **61** to line **62** for blending with the final residue which is withdrawn from the process.

The deoiled residue from extractor **39** is delivered by line **64** to stripper **65**, from whence recovered solvent is returned by lines **66** and **59** to the extractor and stripped residue is delivered to line **62**.

Referring to Fig. II, a straight run residue (reduced crude) is delivered by line **81** to a heating coil **82** in furnace **84**, then by line **85** to a vapor-liquid flash separation section of a flashing tower **86**, having lower and intermediate stripping sections and upper rectifying and condensing sections. The light tops are removed as an overhead vapor stream in line **87**, condensed in condensers **89** and collected in vessel **90**, from whence they are taken as catalytic cracking feed stock. Heavy tops are withdrawn by line **91** as a sidestream from a trap-out tray between the condensing and rectifying sections of the tower, portions being returned above and below the withdrawal point to provide condensation and reflux, the remainder providing additional catalytic cracking feed stock.

Heavy oily asphaltic residue is withdrawn by line **92** from the bottom of the intermediate stripping section of tower **86**, cooled in heat exchangers **94** and **95** and cooler **96** and partially extracted in the upper section of deasphalting tower **97**. The tower **97** is provided at an intermediate level with a plurality of sufficiently extended upright risers **99** extending through and above a horizontal partition member **100**, which provides a collecting zone for partially deoiled asphaltic residue while lighter liquid phase from the lower section is permitted to enter through the risers. Thus, the partial separation of oil and asphalt from the stream from line **92** is effected in the presence of an extract phase obtained by extraction of a cracked product from subsequent thermal cracking of the partially deoiled asphaltic residue recovered from the first stage (upper section) extraction in tower **97**, as described later.

The asphaltic phase which collects on the partition **100** is withdrawn by line **101**, heat exchanged in heat exchanger **102**, stripped of solvent, C_3/C_4 mixture, in asphalt stripper **104**, as by the use of open steam, thermally cracked in cracking coil **105** of furnace **84** and delivered by line **106** to a lower vapor-liquid flash separation zone in tower **86**, located between the lower and upper stripping sections. The vaporized material, together with any steam injected in the bottom stripping section, passes upward through the risers provided in the partition separating the lower and upper stripping sections. The liquid product, after stripping it in the lower section, is collected by extended upright downcomers in the bottom of the tower. This partially deoiled cracked residue is delivered by line **107** and through heat exchangers **102** and **109** and cooler **110** to the lower extraction section of deasphalting tower **97** wherein it is extracted with propane-butane (C_3/C_4) mixture, with the extract phase being delivered to the upper extraction section through risers **99**. By this combination of operations, less desirable oils which are extracted from the cracked residue in the lower section are precipitated as part of the asphalt phase in the upper section, with resultant recycle of them to the cracking step.

The resulting extract phase is withdrawn from tower **97**, through line **111**, heat exchanged in exchangers **109** and **95**, and stripped of C_3/C_4 in oil stripper **112**, with steam, to yield a deasphalted oil in high yield and of good quality as a catalytic cracking feed stock.

The deoiled cracked asphaltic residue from the extraction in tower **97** its withdrawn from the bottom by line **114**, heat exchanged in exchanger **94** and steam stripped in asphalt stripper **115**, to remove the solvent, with the asphalt being removed by line **116**.

Although the placement of auxiliary equipment has been indicated to some extent, some of it has been omitted in order to simplify the drawing and the description of the invention. The placement of various other required or desirable pieces of equipment, such as pumps, valves, compressors, liquid level control devices, flow rate control devices, temperature recorders and control devices, condensers, reboilers, surge and storage tanks, and the like, will be well understood by those skilled in the art to which the invention pertains.

There are several advantageous features incorporated in the particular process as represented in Fig. II, including: (1) the stripping of residue from a flashing operation by vapors from a higher temperature flashing operation performed in the lower section of the same tower; and (2) the stripping of an intermediate asphalt fraction derived principally from a straight run residue, by a mixture of deasphalting solvent (such as liquid C_3/C_4 mixture) and partially or wholly cracked oil derived from deasphalting of cracked residue in a lower section of the deasphalting tower.

A further understanding of various factors involved in the practice of the invention will be had from a consideration of the results to be described with reference to the processing of a reduced crude from Los Angeles Basin crude oil. The properties of a typical flasher pitch withdrawn from a commercial vacuum flasher, operating on Los Angeles Basin reduced crude in the preparation of distillate feed stock for a commercial catalytic cracker, are given in Table 1.

Table 1.—Properties of flasher pitch

Refractive index, *n* (70° C./D)	1.570
Viscosity, 210° F.:	
Centistokes	2060
Saybolt seconds Furol	973
API gravity, 60°/60° F.	7.3
Density:	
d 70° C.	0.9839
d 20° C.	1.015

Table 1—Continued

Coke UV (LHSV=1)	31.8
Molecular weight, av.	800
Elemental, percent w.:	
C	85.60
H	10.56
N	1.15
S	2.28
Sulfate ash, percent w.	0.10

The flasher pitch described in Table 1 was deasphaltized with various light hydrocarbon solvents, such as propane, isobutane, n-butane and isopentane, and in some cases with mixtures thereof. Temperatures used were in the range of 35–130° C. and usually the pressures were essentially equal to the vapor pressure of the solvent at the temperature of operation; however, in some cases inert gas was injected to provide a higher pressure. The solvent-to-feed ratios ranged from 3/1 to 17/1 by volume with about 4/1 being used most frequently. Oil yields were determined, and the coke-on-catalyst values for the oil products were determined for a standard catalytic cracking condition from refractive index (R.I.) and ultraviolet (UV) absorption measurements, the latter being based on fixed bed catalytic cracking experiments. Refractive index determinations have been found to correlate closely with the UV results. Results of these operations are tabulated in Table 2.

Table 2.—Extraction of flasher pitch

Run	Solvent	T, ° C.	P, p.s.i.g.	Solvent / Pitch v./v.	Coke [1] n(70/D)	by: UV	Oil Yield, percent w.
1	Propane	35	175	4.3	10.3	11.0	26.9
2	do	60	320	3.7	7.9		17.7
3	do	60	310	4.3	8.6	9.0	20.0
4	do	80	430	4.3	7.9		8.0
5	do	60	300	4.4	8.6		18.3
6	do	60	320	4.6	7.5		15.3
7	do	60	320	5.0	7.9		14.6
8	do	60	310	8.1	9.0	9.6	22.8
9	do	40	200	8.4	10.2	10.4	33.3
10	do	35	175	8.5	10.2	10.3	36.2
11	do	64	330	9.1	9.3	9.9	29.0
12	do	60	310	9.6	9.3	9.9	22.3
13	i-Butane	60	130	3.1	16.4	16.2	44.8
14	do	60	130	4.0	15.7	15.9	44.0
15	do	40	80	4.0	16.2	15.0	43.0
16	do	60	130	7.4	13.5	14.7	42.5
17	n-Butane	60	90	3.1	21.0		64.8
18	do	80	360	3.7	19.3		63.5
19	do	40	55	3.9	19.6	19.0	61.2
20	do	60	90	4.0	19.4	20.5	60.5
21	do	60	520	4.0	19.8		69.9
22	do	90	520	4.0	16.6		51.9
23	do	130	520	4.0	16.5		36.6
24	do	130	360	4.4	17.8		47.0
25	do	60	300	17.0	16.6		67.2
26	i-Pentane	60		4.0	22.8		72.4
27	n-Butane+Propane (20%w.).	60	140	4.0	18.4		55.0
28	n-Pentane+Propane (40%w.).	60	190	5.4	15.9		44.4

[1] Coke, percent w. at 63% conversion in the catalytic cracking.

The data in Table 2 show that propane extractions gave oil yields in the range of 20–36%, depending on the temperature and solvent/pitch (S/P) ratio. The yields increased with solvent/pitch ratio and with decrease in temperature. Isobutane gave a considerably larger yield of oil, although of poorer quality as catalytic cracking feed stock, as indicated by the coke makes. The results for runs 27 and 28, as compared for example to run 20, indicate that a yield reduction from about 60% down to about 40% results when propane equal to the weight of the butane is added, this 20% increment being available for reflux in a tower deasphalting, particularly where the propane is injected between the butane inlet and butane/oil outlet. Isobutane gave yields intermediate those obtained with propane and with n-butane. Isopentane, even at the solvent/pitch ratio of 4/1 gave an oil yield greater than any obtained with n-butane; the quality of the oil was correspondingly poorer.

Further representative data are given in Table 3 for the deasphalting of the flasher pitch described in Table 1, but counter-currently in a tower provided with forty angularly disposed baffle plates.

Table 3.—Extraction of flasher pitch

Run No.	Solvent	S/P, w./w.	Column temp, ° C.		P, p.s.i.g.	Oil Yield	R.I. coke at 63% conv.	Softening Point of Asphalt, ° C.
			Top	Center and Btm.				
29	Propane	1.71	60	60	360	26.3	7.7	
30	do	1.71	60	60	360	27.6	7.6	87
40	do	1.70	60	60	360	31.1	8.1	
41	do	1.73	80	80	360	15.7	5.2	70
42	do	1.70	60	60	520	19.9	5.4	76
43	do	2.03	50	50	520	28.7	7.5	85
44	n-Butane	1.75	135	135	360	61.2	18.7	132
45	do	2.05	90	90	520	74.6	22.2	159
46	do	4.62	90	90	520	62.1	18.1	
47	i-Pentane	2.50	165	165	465	69.8	21.0	

The yields of oil obtained by the propane deasphalting varied from fifteen to thirty-two percent, with the temperature effect being the most significant factor relating to the yield; higher temperatures gave lower yields of oil of better quality. The effect of butane to feed ratio was reversed from the effect with propane, higher ratios giving lower oil yields. The oil yields obtained with n-butane (thirty-eight to seventy-five percent) were

higher than those for propane. Although the oil yields depend on the solvent used, other factors being constant, selectivities, as indicated by coke values, were essentially the same at equal solvent/feed ratios.

Comparisons have been made between distillates obtained from secondary flashing of the flasher pitch and oil obtained by extraction. The superiority of extracted product as compared to flashed product from pitch becomes less as increased yields (deeper extraction) are obtained. This is indicated qualitatively by the visual observation that oils from propane extraction (deasphalting) produced at low yields are much lighter in color than corresponding flashed products, whereas isopentane extracted oils are somewhat darker in color than corresponding flashed products.

As stated previously, the oil recovered in the first stage extraction for catalytic cracking feed is preferably restricted substantially to that which is extractable with propane alone, so as to maintain it at a high quality level. The same principles apply as well to the subsequent extractions. However, when the subsequent extraction is a separate extraction for maximum oil recovery, with separation of the heavier fraction thereof, as by distillation, and further thermal cracking of it to yield more catalytic cracking feed stock, the extraction is advantageously carried out with a higher hydrocarbon (C_4–C_7) and under conditions to recover the low quality oil components as well.

The advantage of butane extraction of a flash cracked residue over extraction of flasher pitch, both at the same yield, is shown by the improved quality of the deasphalted oil in the former case. For the same quality of oil, the former combination yields the larger volume of oil. The results of extraction of a mildly thermally cracked pitch remaining after flashing off 36.7% by weight light products, and of a flasher pitch remaining after flashing off 39.1% by weight of distillate, both from separate portions of the same straight run residue, are given in Table 4.

Table 4.—Deasphalting flasher pitch and flash cracked residue from L.A. Basin residue

Charge to Deasphalting	Flash Cracked Residue		Flasher Pitch	
DA Run No.	A	B	C	D
DA Conditions:				
Solvent	n-C^4	n-C^4	n-C^4	n-C^4
Solvent/Feed Ratio, vol	3.36	2.82	3.06	3.97
Column Temperature, ° C.:				
Top	129.5	121.1	115.5	121
Bottom	131.1	121.1	115.5	110
Pressure p.s.i.g	525	525	530	395
DA Oil Properties:				
API Gravity at 60° F	14.8	14.4	13.3	14.2
Viscosity, SSU at 210° F	213	233	624.1	448.3
Ramsbottom Carbon Residue, Percent w	6.54	7.10	7.19	7.29
Sulfur, Percent w	1.88	1.92	4.61	2.25
Total Metals, p.p.m	75.8	92.9		
Ni+V, p.p.m	67	81	102	79
Refractive Index, n_D^{70}	1.5282	1.5312		1.5274
Asphalt Properties:				
Penetration, d.m.m. at 77° F	0	0	0	0
Softening Point, ° F	325+	325+	299	268
Specific Gravity	1.135	1.125	1.0824	1.0973
Yields, Percent v., Basis SR Residue:				
Gasoline-Free Distillate	33.6	33.6	40.3	40.3
DA Oil	43.3	46.3	43.0	39.7
Asphalt	18.2	15.0	15.3	18.6

It will be seen that for the same asphalt yield, at two yield levels, the deasphalted oil from the combination of flash cracking plus deasphalting is a superior catalytic cracking feed.

The properties of the gasoline-free distillates in Table 4 are given in Table 5, showing marked reduction in metals content of the flash cracked distillate.

Table 5.—Properties of gasoline-free distillates from flashing and flash cracking of L.A. Basin straight run residue

	Flash Cracking	Flashing
Yield, Percent vol. of SRR	31.5	38.0
API Gravity at 60° F	25.0	23.3
Kinematic Viscosity at 210° F., cs	3.48	4.49
Ramsbottom Carbon Residue, Percent w	0.2	0.3
Sulfur, Percent w	1.29	1.36
Ni+V, p.p.m	<0.003	0.6

The following exemplary processing conditions for a Los Angeles Basin stock are further illustrative of but not limiting on the invention: A 50% topping residue is prepared by the usual distillation topping procedures utilized in the typical refinery. This residue is then vacuum flashed to produce 43% by weight thereof as flasher pitch having a 7.8 API gravity, a 5,000 SSU viscosity at 210° F. and containing 240 p.p.m. of nickel and vanadium, expressed as metal. This flasher pitch is fed to a deasphalting unit using 400% by volume of 50–50 C_3- and C_4-hydrocarbons, based on the flasher pitch. The lower temperature conditions are adjusted to get about 50% of the flasher pitch as asphalt bottoms containing 95–98% of the metals content of the pitch and having a softening point of 250° F. This asphalt is then mildly cracked under conditions to give a substantially lower softening point of the product and to convert the metals to a less soluble form. The mildly cracked asphaltic product is fed to a second deasphalting tower, taking about 50% as bottoms thereof and retaining the major portion of the metals therein.

I claim as my invention:

1. A process for the production and recovery of catalytic cracking feed stock from a reduced crude containing asphaltic and metal-containing constituents and an oil portion which comprises: (1) solvent extracting the reduced crude with a light hydrocarbon deasphalting solvent made up of essentially propane to obtain a solvent extract phase and an asphaltic residue containing an appreciable portion of the oil and a major portion of the metal-containing constituents and recovering predominantly propane-soluble catalytic cracking feed oil components from the solvent extract phase; (2) non-catalytically thermally cracking the asphaltic residue resulting from the extraction at a temperature within the range of about 400° C. to about 500° C. for a period of time selectively chosen within the range of about a few seconds to about 60 minutes so that only mild thermal cracking can take place without the occurrence of appreciable coking, thereby converting the metal-containing components to less oil-soluble metal-containing substances and cracking the asphaltic components to produce paraffinic oil components; (3) extracting from the cracked product by means of the addition of a light hydrocarbon deasphalting solvent comprising essentially a C_4–C_7 hydrocarbon a further amount of propane-soluble components; and (4) recovering predominantly propane-soluble catalytic cracking feed oil components from the resulting solvent extract.

2. A process for the production and recovery of catalytic cracking feed stock from a reduced crude containing asphaltic and metal-containing constituents and an oil portion which comprises: (1) solvent extracting the reduced crude with a light hydrocarbon deasphalting solvent comprising essentially propane to obtain a solvent extract phase and an asphaltic residue containing an appreciable proportion of the oil and a major proportion of the metal-containing constituents and recovering predominantly propane-soluble catalytic cracking feed oil components from the solvent extract phase; (2) non-catalytically thermally cracking the asphaltic residue resulting from the extraction at a temperature within the

range of about 400° C. to about 500° for a period of time selectively chosen from the range of about a few seconds to about 60 minutes so that only a mild thermal cracking can take place without the occurrence of appreciable coking, thereby converting the metal-containing components to less oil-soluble metal-containing substances and cracking the asphaltic components to produce paraffinic oil components; (3) extracting from the cracked product by means of the addition of a light hydrocarbon deasphalting solvent comprising a C_4–C_7 hydrocarbon a further amount of propane-soluble components leaving a propane-insoluble fraction; (4) recovering predominantly propane-soluble catalytic cracking feed oil components from the resulting solvent extract of step (3); and (5) recycling a propane-insoluble fraction derived from the extraction of step (3) to the thermal cracking step (2).

3. An integrated process for the handling of a reduced crude containing asphaltic and metal-containing constituents and an oil portion to produce a quality asphalt and involving the preparation and catalytic cracking of a feed stock derived in an enhanced yield from said reduced crude which comprises (1) solvent extracting the reduced crude with a light hydrocarbon deasphalting solvent to obtain a solvent extract phase and an asphaltic residue containing an appreciable portion of the oil and a major proportion of the metal-containing constituents and recovering predominantly propane-soluble catalytic cracking feed oil components from the solvent extract phase; (2) non-catalytically thermally cracking at least a portion of the asphaltic residue resulting from the extraction at a temperature within the range of about 400° C. to about 500° C. for a period of time selectively chosen from the range of about a few seconds to about 60 minutes so that only mild thermal cracking can take place without the occurrence of appreciable coking, thereby converting the metal-containing components to less oil-soluble metal-containing substances and cracking the asphaltic components to produce paraffinic oil components; (3) extracting from the cracked product by means of the addition of a light hydrocarbon deasphalting solvent a further amount of propane-soluble components; (4) recovering predominantly propane-soluble catalytic cracking feed oil components from the resulting solvent extract of step (3); (5) subjecting the recovered propane-soluble catalytic cracking feed oil components to catalytic cracking without initially hydrogenating said feed oil components and (6) continuously removing from the process a quality asphalt product previously separated from the catalytic cracking feed oil components.

4. A process in accordance with claim 1, wherein the light hydrocarbon solvent used in steps (1) and (3) comprises a substantial proportion of propane.

5. A process in accordance with claim 1, wherein at least a portion of the propane-insoluble metal containing and aromatic components, from which propane-soluble components are separated in steps (3) and (4), is recycled to the thermal cracking step (2).

6. A process in accordance with claim 1, wherein the light hydrocarbon solvent used in steps (1) and (3) comprises a substantial proportion of propane, and wherein the resulting asphaltic residue from the extraction in step (3) is recycled in part to the thermal cracking step (2).

7. A process in accordance with claim 1, wherein the reduced crude which is solvent extracted in step (1) is one from which a substantial portion of distillable catalytic cracking feed oil components has been removed by vaporization at a low subatmospheric pressure while avoiding thermal cracking.

8. A process in accordance with claim 1, wherein the solvent extracting steps (1) and (3) are carried out by countercurrently contacting the extracting agent and the material being extracted, and wherein the extracting agent and oil dissolved therein in step (3) is delivered to step (1) as source of extracting agent.

9. A process in accordance with claim 3, wherein the light hydrocarbon solvent used in steps (1) and (3) is essentially propane and wherein the thermal cracking is carried out at a pressure from about 1 atmosphere to about 500 p.s.i.g.

References Cited in the file of this patent

UNITED STATES PATENTS

2,222,060	Arveson	Nov. 19, 1940
2,559,285	Douce	July 3, 1951
2,696,458	Strickland	Dec. 7, 1954
2,727,853	Hennig	Dec. 20, 1955
2,854,398	Knox	Sept. 30, 1958