(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 026 670**
A2

(12) # EUROPEAN PATENT APPLICATION

(21) Application number: 80303445.3

(22) Date of filing: 30.09.80

(51) Int. Cl.³: C 10 G 1/02
C 10 G 1/08

(30) Priority: 01.10.79 US 80830
01.10.79 US 80831
01.10.79 US 80832

(43) Date of publication of application:
08.04.81 Bulletin 81/14

(84) Designated Contracting States:
BE CH DE FR GB IT LI LU NL SE

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(54) **Process for the production of coke and a liquid product.**

(57) Greater than expected amounts of liquid products are produced by a coking operation in which the feed is composed of a mixture of petroleum residua and shale oil residua. The yield of liquid products is further enhanced by including in the feed a hydrogen catalyst. The yield of liquid products, is still further enhanced by using a hydrocracking catalyst as the hydrogen catalyst and supplying hydrogen to the coking operation. Typical hydrocracking catalysts are NiMo, CoMo, NiW and CoW. which may include an alumina support.

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TITLE MODIFIED
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Title

"Process for Production of Coke and by-products thereof"

The present invention relates to a novel process for producing coke and coke by-products, e.g. liquids such as kerosene and naphta.

In the course of operating a conventional refinery, heavy petroleum streams i.e. petroleum streams having high boiling ranges, are produced as a result of various refinery processes. One of the uses of such material is to form coke, which is a solid carbonaceous material having a number of different uses.

In conventional coking, the heavy refinery stream is heated to elevated temperature, e.g. 468°C (875°F), in the substantial absence of oxygen. As a result, the components of the heavy refinery stream undergo thermal decomposition thereby producing coke and a number of lighter components such as naphtha, kerosene and the like.

Recently, much interest has been focused on the feasibility of producing liquid petroleum products from shale oil, which is an organic semi-solid material similar to crude petroleum and derived from the destructive distillation of the organic matter in oil shale. In order to recover liquid petroleum products from shale oil, the shale oil, like crude petroleum, must be refined. As in the case of refining crude petroleum, refining of shale oil produces a heavy residuum by-product which can if desired by subjected to coking in the same way as heavy petroleum refinery streams.

As appreciated by those skilled in the art of coking, the liquid products produced by the coking operation are normally more valuable than the coke itself. Accordingly, it is desirable to carry-out coking in such a way that the production of liquid products such as naphtha and kerosene is maximized.

It is therefore an object of the present invention to provide a novel coking technique which produces a greater than expected amount of liquid product as compared with conventional coking operation.

We have found, unexpectedly, that the amount of liquid coking product produced is greater than expected if the coking feed is composed of a mixture of a petroleum residuum and a shale oil material, preferably a shale oil residuum.

Accordingly, the present invention provides a coking process which comprises heating a feed material comprising a mixture of a petroleum residuum and a shale oil material in the substantial absence of oxygen to produce coke and a liquid product. An improved yield of liquid products is obtained if the feed material contains a hydrogen catalyst. An even greater improved yield of liquid products can be obtained if the hydrogen catalyst is a hydrocracking catalyst and hydrogen is supplied to the coking operation.

In carrying out the present invention, a mixture of a shale oil material and a petroleum residuum are subjected to coking to produce coke and liquid products, the liquid products being produced in amounts greater than would have been expected.

Coking Procedure

In accordance with the present invention, the coking operation is accomplished in the same way under the same conditions as conventional prior art coking procedures. Thus, in commercial operation the process is normally conducted in a semi-batch mode with the feed stream being continuously fed to the coker and liquid products continuously withdrawn from the coker. Coking of the feed continuously occurs in the coker until the coker is substantially full of coke, at which time the operation is terminated and coke is then removed from the coker.

The operating conditions for the coking operation, as indicated above, are conventional. For example, coking can be conducted at any conventional temperature such as from 315°C (600°F) to (537°C) 1,000°F, preferably about 468°C (875°F). Also, conventional pressures, e.g. atmospheric pressure, can be used. Moreover, the feed stream can be heated while in the coker, although it is preferable to supply all the heat necessary for coking by prehating the feed stream in a furnace or other suitable device prior to entry of the feed stream into the coker.

Shale Oil Material

As the shale oil material used in the inventive process, shale oil in any form, or any component part thereof, can be used. In this regard, crude shale oil as indicated above is normally obtained in the form of a solid or semi-solid material. This material, when heated to a temperature high enough to become liquid, can itself be used as the shale oil material. This material, when heated to a temperature high enough

to become liquid, can itself be used as the shale oil material. Alternatively, the shale oil can be first hydrocracked to form a liquid shale oil product, and this liquid shale oil product used as the shale oil material. However, since it is easier and more economic to recover the light products from shale oil (be it crude shale oil or hydrocracked shale oil) prior to coking, it is preferred that the shale oil material used in the inventive process be composed of a shale oil residuum, i.e. the bottom or lower end of the shale oil.

In other words, it is contemplated that in the normal course of refining shale oil, be it crude shale oil or hydrocracked shale oil, most of the light ends of the shale oil will be removed by conventional refining techniques. The remaining fraction of the shale oil, the shale oil residuum, which will normally represent the bottom 60%, preferably 50%, of the shale oil, can ideally be used as the shale oil material in accordance with the present invention. For example, it has been found most convenient to use a (371°C+) 700°F+ fraction of shale oil, which represents the bottom 54% by weight of the shale oil, as the shale oil material in accordance with the present invention.

Petroleum Residuum

As the petroleum residuum useful in accordance with the present invention, any petroleum derived refinery stream capable of undergoing any significant coking can be used. Such materials can be described as petroleum-derived refinery streams in which a minimum of 80% by weight boils above 315°C (600°F). Preferred petroleum residua

are those in which a minimum of 80% boils above 371°C (700°F), most preferably 537°C (1,000°F).

For example, a preferred petroleum residuum is the distillation residue recovered as the bottom stream from a conventional vacuum distillation column. This material, commonly known as vacuum tower bottoms, has a boiling range such that a minimum of 80% boils above 537°C (1,000°F). Another petroleum refinery stream that can be used as the petroleum residua is the bottoms products of an atmospheric distillation column, which is normally characterized as having 80% boiling above 371°C (700°F). Still another petroleum refinery stream which is ideally suited as the petroleum residuum in accordance with the present invention is a decanted oil which is the bottoms products produced by distilling the effluent of a fluid catalytic cracker. And is well known, decanted oil is a highly aromatic material having a low API gravity and a boiling range such that 80% boils above 315°C (600°F), preferably 371°C (700°F), and is ideally suited for use as a coker feed.

Moreover, in accordance with the present invention, the petroleum residuum component of the feed may be composed at least in part of organic matter derived from non-petroleum sources. For example, the petroleum material may include some bitumen from tar sands and/or pulverized coal. Essentially any amounts of bitumen can be included in the petroleum residuum while the amounts of pulverized coal in the petroleum residuum should be no more than about 50% by weight, based on the combined weight of the coal and petroleum residuum.

Relative Proportions

In accordance with the present invention, it has been found that an unexpected increase in the amount of liquid product produced by coking will be realized when a shale oil residuum and a petroleum residuum are mixed in any proportions. Preferably, however, the amount of shale oil material in the feed mixture is 5 to 85 weight percent based on the total weight of the feed mixture, with shale oil concentrations in the amounts of 15 to 50% and more particularly 20 to 30% being especially preferred.

Use of Hydrogen Catalyst

In a preferred embodiment of this invention, a suitable catalyst is included in the feed introduced into the coker. As suitable catalysts, any material which will catalyze the reaction of hydrogen (be it molecular, atomic or combined) with free radical organic compounds and/or unsaturated organic compounds can be used. Such catalysts are referred to herein as "hydrogen catalysts".

Many types of hydrogen catalysts are known. One well known type of hydrogen catalyst is referred to in the art as a hydrogen transfer catalyst. Hydrogen transfer catalysts are known to catalyze the addition of molecular or combined hydrogen to a free radical organic compound, usually a hydrocarbon. Such catalysts are normally used in co-liquefaction when combined hydrocarbon from one organic compound is transferred to another free radical organic compound. Examples of known hydrogen transfer catalysts are iron pyrites and alkaline iron oxide.

The second type of hydrogen catalysts that can be employed in the inventive process is known in the

art as a "hydrogenation catalyst". Such catalysts are normally used to add molecular hydrogen across an unsaturated double bond, although they can also be used for hydrogenating aromatically unsaturated compounds. Well known examples of this type of catalysts are metallic nickel, platinum and palladium.

A third and preferred type of hydrogen catalyst useful in the inventive process is known as a "hydrocracking catalyst." Such catalysts are normally used in petroleum refining and function both to cleave a large organic molecule into smaller organic molecules and at the same time to add hydrogen to each of the sites where the break occurred. Examples of well known hydrocracking catalysts are NiMo, CoMo, NiW and CoW. Preferred hydrocracking catalysts are NiW and NiMo. Such catalysts are usually supported on alumina supports.

It has also been found that the sulfur and nitrogen contents of process feed materials are usually reduced when a catalyst is used in accordance with the present invention.

The amount of catalyst employed in this embodiment is not critical and can vary between wide limits. From an economic feasibility standpoint, the amount of catalyst should probably be no more than about 10 weight percent based on the weight of coker feed, and consequently the amount of catalyst in the feed material will normally be between greater than 0 to 10 percent by weight. The preferred amount of catalyst is 0.01 to 5 weight percent with the most preferred amount of catalyst being 0.05 to 1 weight percent.

It is preferred that the coking operation be carried out so that the catalyst is at least partially

mixed with the feed material undergoing coking. In this regard, it has been noticed in using a laboratory scale batch coker that the catalysts will normally settle to the bottom of the coker if the liquid therein is quiescent. Thus, if coking is accomplished in a strictly batch operation, it is preferably to mix the liquid in the coker during the coking operation so that the catalysts will be distributed throughout the mass of liquid undergoing coking. Mixing can be accomplished by any conventional means such as using a mechanical mixer or passing an inert gas through the liquid.

Commercially, coking is usually accomplished in a semi-batch operation wherein liquid feed is continuously fed to the "delayed coker" and liquid products continuously removed from the coker. The liquid fed in the coker during the coking operation continues to be converted to coke and liquid product until the coker substantially fills with solid coke at which time the coking operation is terminated. In such an operation, feeding the liquid feed to the coker inherently causes enough mixing to provide reasonable distribution of the catalyst in the liquid feed being coked.

In accordance with one feature of this embodiment, catalysts which have been previously used in the inventive process can be recycled for reuse. This can be accomplished in two ways. In accordance with one technique, coke product containing the catalyst therein after suitable comminution can itself be returned to the coker with fresh feed. In accordance with the other technique, coke product containing the catalyst therein is subjected to combustion, thereby freeing

the catalyst in the form of an ash by-product. The ash by-product can then be returned to the coker with fresh feed. Recycling of catalyst has the obvious advantage of reducing the total amount of catalyst required.

Use of a Hydrocracking Catalyst and Hydrogen

In another, more preferred embodiment of this invention, the yield of liquid products can be enhanced by using as the hydrogen catalyst, a hydrocracking catalyst and by supplying hydrogen to the coking operation, i.e. supplying hydrogen to the feed material while the feed material is being heated. The hydrocracking catalysts here used have been described earlier. Hydrogen transfer catalysts as well as hydrogenation catalysts, which were also described earlier, can be included in the coking operation, i.e. reaction system, but even in this event, it is still necessary to include a hydrocracking catalyst in the coking operation to be within the description of this preferred embodiment. Examples of hydrocracking catalysts which have been found to be especially useful in accordance with the present invention are NiMo, NiW, CoMo and CoW. Such catalysts are usually supported on alumina. Of these catalysts NiMo and NiW supported on alumina are especially preferred.

The amount of hydrocracking catalyst to be included in the reaction system can vary widely. Broadly, the amount of hydrocracking catalyst can be between greater than 0 to 10 weight percent. More preferably, the amount of cracking catalyst is between 0.01 to 5 weight percent with amounts on the order of 0.05 to 1 weight percent being most preferred.

Coking is accomplished in a conventional manner in accordance with this embodiment with the exception that hydrogen is supplied to the reaction system during the coking operation.

Hydrogen can be supplied to the reaction system in any convenient manner. Most conveniently, suitable inlet orifices will be provided in the coking apparatus for the advent of the hydrogen. Since it is preferable that the hydrocracking catalyst be reasonably well mixed in the reaction system during the coking operation, it is preferred that the hydrogen be introduced so as to cause turbulence of the liquid reaction system, thereby causing significant mixing. The hydrogen can be introduced in other ways, of course, in which case it is preferable to provide other means, e.g. mechanical stirrer, for causing mixing of the liquid reaction system. Hydrogen may also be produced in situ in the reactor by feeding steam thereto, the steam reacting with the coke and/or light hydrocarbons in the system to generate hydrogen.

The amount of hydrogen fed to the reaction system can also vary over wide limits. Broadly, the total amount of hydrogen supplied during a particular coking operation can be to 30 SCF/lbs liquid feed (125 to 1970 cc/g). Preferably, the amount of hydrogen fed is 5 to 15, (312 to 936 cc/g) most preferably 12 to 15 (748 to 936 cc/g) SCF/lbs liquid feed.

Although this embodiment can be carried out at widely varying pressures, it is preferred to operate at conventional coking pressures, i.e. greater than 0 to about 7 kg/cm^2 gauge (100 psig). Such pressures it will be noted are much less than

occurring in conventional petroleum hydrocracker units wherein the pressure is on the order of 140 kg/cm^2 gauge 2,000 psig. Preferred operating pressures in the inventive process are on the order of 1.75-6.3 kg/cm^2 gauge (25 to 90 psig). If desired, inert gases such as nitrogen can also be included in the reaction system.

WORKING EXAMPLES

In order to more thoroughly describe the present invention, the following working examples are presented.

In these examples, coking was accomplished in a batch operation using a laboratory scale coker (mini-coker) composed of a carbon steel reaction vessel defining a cylindrical reaction compartment having a diameter of 10 cms (4 inches) and an internal height of 53 cms (21 inches). A feedline was connected to the bottom of the mini-coker for the introduction of feed material and an exit line was attached to the top of the mini-coker for withdrawal of gaseous and liquid products during the coking operation. In order to prevent condensation of the liquid product in the outlet line, the outlet line was heated to a temperature of 343°C (650°F) during the coking operation. In each example, 2,000 grams of feed was charged into the mini-coker and the pressure in the mini-coker maintained at 6.3kg/cm^2 gauge (90 psig) and the mini-coker heated using a 48 hour thermal cycle shown in the following Table 1. In each example, the liquid product obtained consisted predominantly of kerosene and naphtha.

TABLE I

Temp., °F	°C	Time Hours	Total on-Stream Time Hours
75	24	0.0	0.0
600	315	1.0	1.0
650	343	8.0	9.0
750	398	12.0	21.0
850	454	0.5	21.5
860	460	0.5	22.0
860	460	9.0	31.0
900	482	11.0	42.0
920	493	1.0	43.0
940	504	1.0	44.0
1,100	593	1.5	45.5
1,200	648	2.5	48.0

The feed materials employed were a decanted oil, a vacuum tower bottoms, and a 371°C+ (700°F+) fraction of shale oil, which represents the bottom 54% of whole shale oil. The following Table II shows the properties of these materials.

TABLE II

	Shale Oil Bottoms	Decanted Oil	Vacuum Bottoms
°API	14.60	-0.20	11.90
Wt. % Sulfur	0.55	1.34	1.25
Wt. % Nitrogen	2.32	0.12	0.36
Wt. % Ash	0.062	0.050	--

Examples 1 to 3 and Comparative Examples A and B

In Examples 1 to 3, mixtures of the above-described shale oil residuum and the above-described decanted oil were subjected to coking. In addition, for the purposes of comparison a feed comprising all

shale oil residuum and a feed comprising all decanted oil were also coked. The composition of the feed materials plus the results obtained are set forth in the following Table III. Unless otherwise indicated, all numbers in this and following table are in weight percent.

TABLE III

EFFECT OF FEED COMPOSITION ON PRODUCT YIELDS

Example	Feed Composition		Liquid Product Yields*		
	Shale Oil	Decanted Oil	Experimental	Calculated	E-C
Comp A	0	I00	15.40		
1	25	75	33.68	23.68	10.00
2	50	50	37.20	31.97	5.23
3	75	25	43.12	40.25	2.87
Comp B	100	0	48.53		

Contd...

Example	Coke Yields		
	Experimental	Calculated	E-C
Comp A	61.I2		
1	46.27	52.73	-6.46
2	44.05	44.34	-0.29
3	35.42	35.95	-0.53
Comp B	27.56		

*Liquid Product Yields includes coke volatiles

From the foregoing, it can be seen that the amount of liquid product yields realized when a mixture of a shale oil residuum and decanted oil are employed as the feed is significantly greater than would have been expected based on the amount of liquid product obtained when only shale oil residuum and only decanted oil are coked. Moreover, it will be noticed that the amount of coke produced is less than would have been expected, although not as much less as the unexpected increase in the amount of liquid product yields. Inasmuch as liquid products of the coking operation are more valuable than the coke, this is a significant commercial advantage.

Example 4 and Comparative Examples C and D

The procedures used in Examples 1 to 3, Comparative Example A and Comparative Example B were repeated except that a vacuum tower bottoms was used in place of the decanted oil as the petroleum residuum. The composition of the feed as well as the results obtained are set forth in the following Table IV.

TABLE IV

EFFECT OF FEED COMPOSITION ON PRODUCT YIELDS

Example	Feed Composition		Liquid Product Yields*		
	Shale Oil	Vacuum Bottoms	Experimental	Calculated	E-C
Comp C	0	100	46.70		
4	50	50	49.30	47.62	1.68
Comp D	100	0	48.53		

Contd...

Example	Coke Yields		
	Experimental	Calculated	E-C
Comp C	29.95		
4	28.32	28.76	-0.44
Comp D	27.56		

*Liquid Product Yields includes coke volatiles

From the foregoing, it can be seen that an unexpected increase in liquid product yields is also realized when the petroleum residuum is a vacuum tower bottoms.

Use of a Hydrogen Catalyst

In order to more thoroughly describe this embodiment, the following working examples are presented.

In each of these examples, a mini-coker as described earlier was used. In carrying out the examples, the catalyst was first pulverized (particle size less than 100 mesh) and then mixed with the feed material prior to its introduction into the coker. The pressure was varied from 0 to 6.3 kg/cm^2 gauge (0 to 90 psig) which is the normal range of operation for a commercial delayed coker. The coker was then heated to elevated temperature in accordance with the programmed temperature cycle shown in the following Table V.

TABLE V

Time at Temperature in the Mini-Coker

Temp., °F	°C	Time, Minutes
600	315	45
800	426	45
900	482	30
1,000	537	30
1,100	593	30
1,200	648	90

In order to prevent condensation and reflux of a liquid product, the outlet line of the mini-coker was heated to 343°C (650°F) prior to the start

of each test. The volume of the offgas was measured and samples were taken at regular intervals for analysis. In the tests where a catalyst was used, its weight was not included in the material balance calculations. Since the volatile matter remaining in the coker could vary over wide limits, the yield of coke was calculated on a 0 VCM (volatile carbonaceous matter) basis. This volatile matter was included in the liquid product as was the C_4+ material in the gas stream for material balance purposes.

Examples 5 and 6 and Comparative Examples E and F:

Three catalyst types were tested for their effect on liquid product yields. These were a fluid catalytic cracking catalyst, a hydrogen transfer catalyst and a hydrocracking catalyst. In these tests, no effort was made to keep the catalyst suspended during the cracking process. The indentity of the catalyst, the composition of the feed, other variables and the results obtained are set forth in the following Table VI.

TABLE VI

Effect of Catalyst Type on Product Yield and Sulfur and Nitrogen Contents

Feed: 50% Whole Shale Oil, 50% Vacuum Tower Bottoms
Catalyst Concentration: 1.0 wt. % of feed
Pressure: 25 psig

Example	Catalyst		Product Yields Wt. %	
	Type	Composition	Liquid, C_4+	Coke* (0 VCM)
Comp E	None	---	63.23	23.36
Comp F	FCC		63.03	26.82
5	H Transfer	Iron Pyrites	64.79	24.67
6	Hydrocrack		67.16	22.56

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Example	Total Product -S & N Contents Wt. %	
	S	N
Comp E	1.79	1.58
Comp F	1.65	1.63
5	1.64	1.50
6	1.66	1.24

*Catalyst weight not included.

From the above Table VI, it can be seen that the amount of liquid yields produced when a hydrogen transfer catalyst or a hydrocracking catalyst are included in the feed material is significantly above the yield obtained when no catalyst or a catalyst not having a hydrogenation capability, i.e. a conventional fluid catalytic cracking catalyst, are used.

Examples 7 and 8

The laboratory scale coking apparatus used in the foregoing examples was modified so that a gas could be tangentially introduced at its base to ensure that the catalyst remains suspended during coking. Example 6 was repeated twice, in one instance nitrogen gas being fed at a rate of about 0.02 ft^3/minute to the coker and in the other instance no nitrogen being fed to the coker. The results obtained are set forth in the following Table VII.

TABLE VII

Effect of Keeping the Catalyst Suspended with Nitrogen

50% Whole Shale Oil
50% Vacuum Bottoms
1% Hydrocracking Catalyst, Based on Feed
25 Psig (1.75 kg/cm^2 gauge)

Products	Example 7 Catalyst Suspended	Example 8 Catalyst Not Suspended
Liquid (C_4+), Wt. %	72.84	67.91
Coke (0 VCM)*, Wt. %	20.24	19.48
Total Products		
S, Wt. %	1.70	1.56
N, Wt. %	1.50	1.73

* Catalyst weight not included.

From Table VII, it can be seen that mixing of the liquid feed undergoing coking to ensure a reasonable distribution of the catalysts therein causes liquid products to be produced in even higher yields.

Examples 9 to 13 and Comparative Example G:

Five Different hydrocracking catalysts were used in the inventive process. The conditions of use as well as the results obtained are set forth in the following Table VIII.

TABLE VIII

Effect of Hydrocracking Catalyst Type

50% Whole Shale Oil
50% Vacuum Bottoms
Catalyst Concentration: 1 Wt. % Based on Feed
25 psig (1.75 kg/cm^2 gauge)
Suspending Gas: Nitrogen

Example	Catalyst*	Product Yields, Wt. % liquid (C_4+)	Coke** (0.VCM)	Total Product S&N Wt. % S	N
9	4.1% Ni 13.3% Mo	72.84	20.24	1.70	1.50
10	2.7% Ni 50.3% W	71.44	18.71	1.73	1.58
11	2.9% Ni 17.5% Mo	70.73	19.48	1.76	1.54
12	5.8% Ni 27.2% W	72.39	24.01	1.94	1.60
13	6.6% Ni 29.1% W	70.43	19.39	1.87	1.52
Comp G	None	70.26	18.75	1.72	1.64

*Wt. %, all catalysts supported on SiO_2 stabilized alumina.

** Catalyst weight not included.

From the above Table VIII, it can be seen that all the hydrocracking catalysts provide improvement in the yields of liquid product obtained. Moreover, hydrocracking catalysts of the NiW type (Examples 9 and 12 show an excellent increase in the amount of liquid product yields.

Examples 14 to 16

In order to determine the effect of pressure on this embodiment, three additional examples were conducted using the hydrocracking catalyst of Example 9. The conditions of the examples as well as the results obtained are set forth in the following Table IX.

TABLE IX

Effect of Pressure

Suspending Gas: Nitrogen
50% Whole Shale Oil
50% Vacuum Bottoms
Hydrocracking Catalysts Concentration: 1 wt. %

Example	14	15	16
Pressure, psig	25.00	50.00	90.00
kg/cm^2 gauge	1.75	3.50	6.30
Wt. % Liquid (C_4+)	72.84	72.13	70.07
Wt. % Coke* (0 VCM)	20.24	19.19	21.86
Total Product			
S, Wt. %	1.70	1.76	1.87
N, Wt. %	1.50	1.54	1.42

*Catalyst weight not included

As can be seen from the above table, improved liquid yields are obtained over the entire conventional range of commercial coking operations,

i.e. about 25 to 90 psig (1.75 6.30 kg/cm^2 gauge).

Examples 17 to 21 and Comparative Example H and I:

In order to determine the effect of feed composition on the liquid product yields, an additional series of experiments was conducted. In these experiments, the ratio between the shale oil component and the petroleum component of the feed were varied, these examples using the hydrocracking catalyst of Example 9 present in an amount of 1% by weight in each feed. The conditions of the examples as well as the results obtained are set forth in the following Table X.

TABLE X

EFFECT OF FEED COMPOSITION ON LIQUID YIELD

Suspending Gas: N_2

1% Hydrocracking Catalyst

25 Psig

Example	Feed Composition Wt.% Shale Oil	Vacuum Bottoms	Liquid (C_4+) Yield, Wt. % Experimental	Calculated	E-C
Comp H	0.00	100.00	57.41		
17	10.24	89.76	62.27	59.94	2.33
18	25.26	74.74	69.20	63.64	5.56
19	50.00	50.00	72.84	69.74	3.10
20	74.37	25.63	78.11	75.75	2.36
21	88.87	11.13	78.62	79.33	-0.71
Comp 1	100.00	0.00	82.07	--	--

Contd...

Example	Feed Compositions Wt. % Shale	Wt. % Vacuum Bottoms
Comp H	0.00	100.00
17	10.24	89.76
18	25.26	74.74
19	50.00	50.00
20	74.37	25.63
21	88.87	11.13
Comp 1	100.00	0.00

From the foregoing, it can be seen that the greatest increase in the amount of liquid products obtained is when the shale oil component of the feed is about 25 wt. %.

Use of Hydrocracking Catalyst and Hydrogen

In order to more thoroughly describe this embodiment, the following working examples are presented.

The data presented in these examples was obtained in the benchscale, batch mini-coker described earlier. In the mini-coker, the nominal charge of feed material is 2,000 g. In these tests where a catalyst was used, the catalyst was first pulverized and mixed with the feed material prior to its introduction into the mini-coker. To keep the catalyst suspended, a stream of gas was introduced at the base of the coker. The pressure was maintained at 25 psig 1.75 kg/cm^2 for all tests. The program temperature cycle, shown in Table XI below, was developed specifically for use with vacuum tower bottoms.

TABLE XI

TIME AT TEMPERATURE IN THE MINI-COKER

Temp, °F	°C	Time, Minutes
600	315	45
800	426	45
900	482	30
1,000	537	30
1,100	593	30
1,200	648	90

Temperature changes were made as rapidly as possible. The total elapsed time generally ranged

from 6.5 to 7 hours. The overhead (distillate) line was heated to 343°C (650°F) prior to the start of each test to minimize reflux (recycle). The volume of the offgas was measured and samples were taken at regular intervals for analysis. Hydrogen and nitrogen were calculated out of the gas analysis when they were used to suspend the catalyst. In those tests in which a catalyst was used, its weight was not included in material balance calculations. Since the volatile matter remaining in the coke could vary over rather wide limits, the yields of coke were generally calculated on a 0 VCM basis. This volatile was included in the liquid product as was the C_4+ material in the gas stream for material balance purposes.

Examples 22 to 24 and Comparative Examples J and K:

Whole shale oil was coked in a mini-coker while the gas, usually hydrogen, was fed to the coker. In Examples 22 to 24, three different hydrocracking catalysts were included in the feed mixture. In Comparative Examples J and K, no catalyst was included in the system. The identity of the catalysts and the results obtained are set forth in the following Table XII.

TABLE XII

EFFECT OF HYDROCRACKING CATALYST
Feed: Whole Shale Oil

Example	Comp J	Comp K	22	23	24
Catalyst*	None	None	2.9% Ni 17.5% Mo	4.1% Ni 13.3% Mo	2.7% Ni 50.3% W
Wt. %	--	--	1.00	1.00	1.00
Suspending Gas	N_2	H_2	H_2	H_2	H_2
Products					
Wt. % Liquid (C_{4+})	79.17	77.42	82.04	84.05	84.56
Wt. % Coke (0 VCM)**	10.15	9.31	8.65	6.43	9.93
Products, % S					
Liquid	0.65	0.68	0.63	0.61	0.65
Coke	0.49	0.47	2.27	0.80	0.43
Liquid + Coke	0.63	0.65	0.86	0.64	0.62
Products, % N					
Liquid	2.21	2.48	2.22	2.26	2.26
Coke	3.77	3.82	3.73	3.32	3.50
Liquid + Coke	2.42	2.69	2.43	2.41	2.43

*Supported on Alumina.

** Catalyst Weight not included.

From the foregoing, it can be seen that all three hydrocracking catalysts show increased liquid product yields when hydrogen is added. Without a catalyst, hydrogen had no beneficial effect. None

of the catalysts had any significant effect on product sulfur and nitrogen.

Examples 25 to 27 and Comparative Examples L and M:

Examples 22 and 24 and Comparative Examples J and K were repeated except that the feed consisted of a mixture of 50% whole shale oil and 50% vacuum tower bottoms. The identity of the catalysts as well as results obtained are set forth in the following Table XIII.

TABLE XIII

EFFECT OF HYDROCRACKING CATALYST
Feed: 50 Wt. % Whole Shale Oil, 50 Wt. % Vacuum Bottoms

Example	Comp L	Comp M	25	26	27
Catalyst*	None	None	2.9% Ni 17.5% Mo	4.1% Ni 13.3% Mo	2.7% Ni 50.3% W
Wt. %	--	--	1.00	1.00	1.00
Suspending Gas	N_2	H_2	H_2	H_2	H_2
Products					
Wt. % Liquid (C_4+)	73.74	73.75	79.63	76.28	76.74
Wt. % Coke (0 VCM)**	15.34	15.81	14.50	13.87	13.85
Products, % S					
Liquid	0.57	0.64	0.62	0.62	0.62
Coke	2.00	2.01	1.95	1.91	1.98
Liquid + Coke	0.96	0.97	0.93	0.92	0.94
Products, % N					
Liquid	1.30	1.31	1.31	1.41	1.37
Coke	1.49	1.71	1.58	1.58	1.67
Liquid + Coke	1.35	1.41	1.37	1.45	1.44

*Supported on Alumina.

** Catalyst weight not included.

From the foregoing, it can be seen that hydrogen without a catalyst has no effect on liquid product yields. All three catalysts, however, result in increased liquid yields when hydrogen is added to the coking mixture. Total product sulfur also decreased, but product nitrogen remained essentially the same.

Examples 28 to 31:

A feed mixture comprising 50 weight percent whole shale oil and 50 weight percent vacuum tower bottoms was coked in the mini-coker while about 1 liter/min. H_2 gas was fed thereto. The reaction pressure was 1.75 kg/cm^2 (25 psig). In each example, a catalyst comprising 2.9% Ni, 17.5% Mo was used, the amount of catalyst in the feed mixture being varied. The amount of catalyst in each example and the results obtained are set forth in the following Table XIV.

TABLE XIV

EFFECT OF HYDROCRACKING CATALYST CONCENTRATION
Feed: 50 Wt. % Whole Shale Oil
50 Wt. % Vacuum Bottoms, Suspending Gas: H_2

Example	28	29	30	31
Wt. % Catalyst	1.00	0.50	0.25	0.05
Products				
Wt. % Liquid (C_4+)	79.63	77.79	78.83	78.78
Wt. % Coke (0 VCM)*	14.50	15.41	12.90	13.35
Products, % S				
Liquid	0.62	1.06	0.63	0.66
Coke	1.95	3.28	1.79	2.05
Liquid + Coke	0.93	1.63	0.91	0.99
Products, % N				
Liquid	1.31	1.44	1.43	1.32
Coke	1.58	2.04	1.75	1.79
Liquid + Coke	1.37	1.59	1.51	1.43

*Catalyst weight not included.

As can be seen, very low concentrations of catalysts are effective when hydrogen is also supplied to the reaction system. Yield structure and product sulfur and nitrogen were very similar when using from 0.05 to 1.00 weight percent hydrocracking catalyst.

Examples 32 and 33:

In one feature of this embodiment, used catalysts can be recycled for reuse. Example 33 illustrates this procedure, while Example 32 using fresh catalyst is presented for purposes of comparison. In Examples 32 and 33 the feed consisted of 50 weight percent whole shale oil and 50 weight

percent vacuum bottoms together with 1.00 weight percent catalysts. In Example 32, fresh catalyst was employed and the feed was coked to produce a liquid product and coke. The coke product of Example 32 was removed from the coker and combusted in air to produce an ash product containing used catalyst. Enough ash product was added to an additional amount of feed material so that the catalyst content thereof was one weight percent. This feed material was then coked again as example 33. The results obtained are set forth in the following Table XV.

TABLE XV

EFFECT OF RECYCLING HYDROCRACKING CATALYST
Feed: 50 Wt. % Whole Shale Oil,
50 Wt. % Vacuum Bottoms, Suspending Gas: H_2

Example	32	33
Catalyst (4.1% Ni, 13.3% Mo)	Fresh	Recycled
% Active (based on fresh feed)	1.00	1.00
Products		
Wt. % Liquid (C_4+)	76.28	74.97
Wt. % Coke (0 VCM)*	13.87	16.24
Products, % S		
Liquid	0.62	1.09
Coke	1.91	3.55
Liquid + Coke	0.92	1.75
Products, % N		
Liquid	1.41	1.46
Coke	1.58	2.09
Liquid + Coke	1.45	1.63

* Catalyst weight not included.

It will be noted that the yield structures of Examples 32 and 33 are quite similar, although the recycled catalyst gave slightly less liquid and more coke. The recycled catalyst does result in higher product sulfur and nitrogen.

Examples 34 and 35:

Examples 32 and 33 were repeated except that coke produced in Example 32 was used in Example 35 without burning to produce an ash. In other words, the coke products of Example 34 were used as the catalyst source. Also, the amount of coke added to the feed of Example 35 was such that the amount of catalyst therein was 0.34 weight percent rather than 1.00 weight percent. The results obtained are set forth in the following Table XVl.

TABLE XVI

EFFECT OF RECYCLING COKE CONTAINING HYDROCRACKING CATALYST
Feed: 50 Wt. % Whole Shale Oil, 50 Wt. % Vacuum Bottoms, Suspending Gas: H_2

Example	34	35
Catalyst (2.9% Ni, 17.5% Mo)	Fresh	Recycled
% Active (based on fresh feed)	1.00	0.34
Products		
Wt. % Liquid (C_4+)	79.63	79.32
Wt. % Coke (0 VCM)*	14.50	19.97
Products, % S		
Liquid	0.62	0.63
Coke	1.95	1.92
Liquid + Coke	0.93	0.97
Products, % N		
Liquid	1.31	1.35
Coke	1.58	1.62
Liquid + Coke	1.37	1.42

* Catalyst weight not included.

As can be seen, liquid yields are same whether fresh or recycled catalyst is used. Coke yield is somewhat higher in the case of recycled catalysts. Also, product sulfur and nitrogen are also slightly higher with recycled catalyst.

CLAIMS

1. A process comprising heating a feed material comprising a mixture of a petroleum residuum and a shale oil material in the substantial absence of oxygen to produce coke and a liquid product.

2. A process as claimed in claim 1 characterised in that the shale oil material is a shale oil residuum.

3. A process as claimed in claim 2 characterised in that shale oil residuum is composed of no more than the bottom 60 weight percent of shale oil.

4. A process as claimed in any of claims 1 to 3 characterised in that it comprises 5 to 85% shale oil residuum.

5. A process as claimed in any of claims 1 to 4 characterised in that the petroleum residuum has a boiling range such that a minimum of 80% of said petroleum residuum boils above 315°C (600°F).

6. A process as claimed in any of claims 1 to 5 characterised in that the feed material contains a hydrogen catalyst.

7. A process as claimed in claim 6 characterised in that the feed material contains up to 10 weight % hydrogen catalyst.

8. A process as claimed in claim 6 or claim 7 characterised in that the hydrogen catalyst is a hydrogen transfer catalyst.

9. A process as claimed in claim 8 characterised in that the hydrogen transfer catalyst is iron pyrites.

10. A process as claimed in claim 6 or claim 7 characterised in that the hydrogen catalyst is a hydrogenation catalyst.

11. A process as claimed in claim 10 characterised in that the hydrogenation catalyst is selected from metallic nickel, platinum and palladium.

12. A process as claimed in claim 6 or claim 7 characterised in that the hydrogen catalyst is a hydrocracking catalyst.

13. A process as claimed in claim 12 characterised in that the hydrocracking catalyst is selected from NiMo, CoMo, NiW and CoW.

14. A process as claimed in claim 13 characterised in that the hydrocracking catalyst include an alumina support.

15. A process as claimed in any of claims 1 to 14 characterised in that the feed material containing said hydrogen catalyst is mixed during coking.

16. A process as claimed in any of claims 1 to 15 characterised in that it includes the step of withdrawing coke from the reaction zone wherein coking has occurred, mixing the hydrogen catalyst contained in said coke with additional feed material and subjecting said additional feed material to coking.

17. A process as claimed in any of claims 1 to 6 characterised in the feed material the hydrogen catalyst which is the hydrocracking catalyst and hydrogen is supplied to the feed material while the feed material is being heated.

18. A process as claimed in claim 17 characterised in that the feed material contains up to 10 weight percent hydrocracking catalyst.

19. A process as claimed in claim 18 characterised in that the shale oil material comprises whole shale oil.

20. A process as claimed in claim 19 characterised in that the shale oil material comprises the bottom 60% or less of whole shale oil.