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COMBINATION FLUIDIZED SOLIDS PROCESS FOR
PRODUCING FUELS AND CHEMICALS
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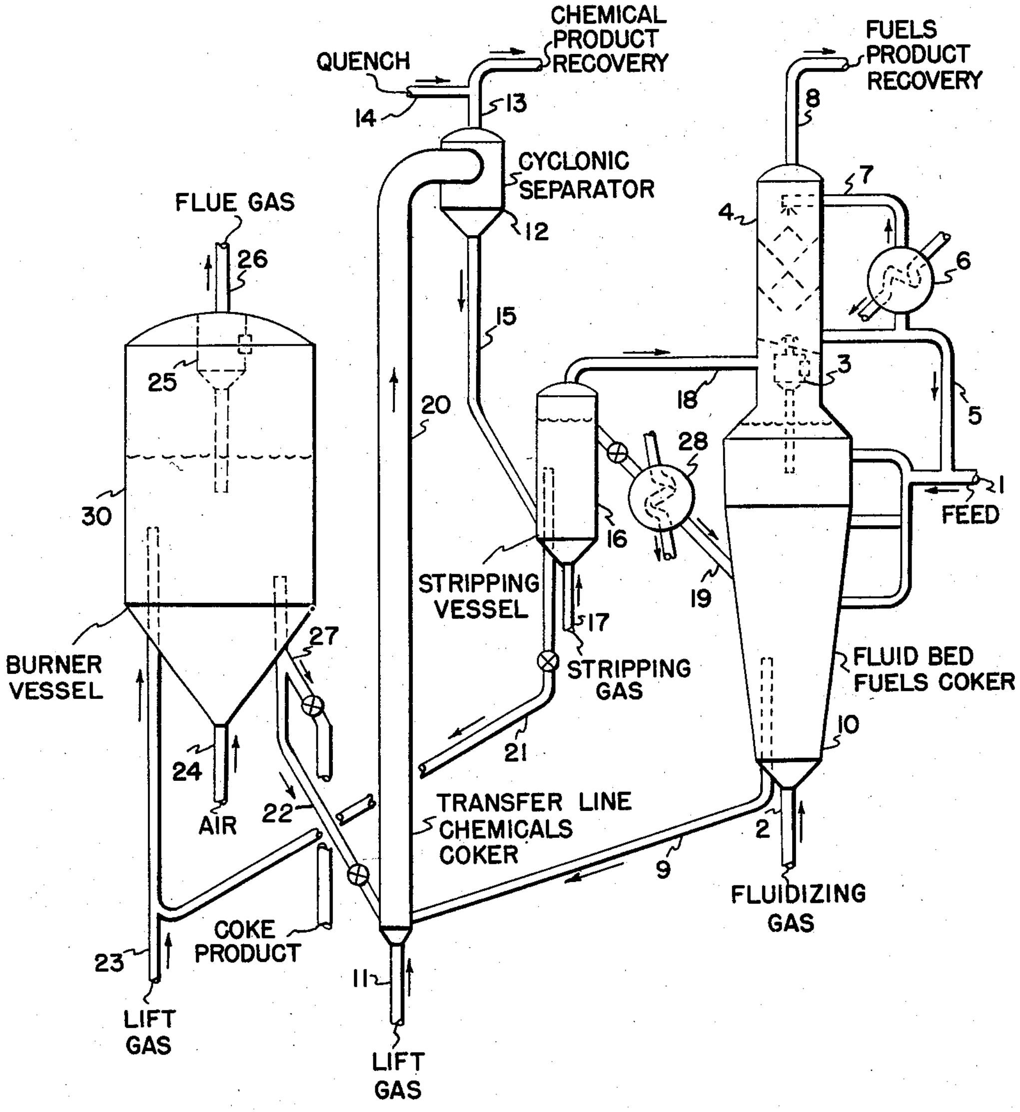

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COMBINATION FLUIDIZED SOLIDS PROCESS FOR PRODUCING FUELS AND CHEMICALS

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3 Claims. (Cl. 202—20)

This invention pertains to the conversion of hydrocarbons by pyrolysis. More particularly, it is concerned with a fluidized solids process for producing normally liquid hydrocarbon distillates suitable for use as fuels and as catalytic cracking feed stocks, and for producing hydrocarbons suitable for use as chemicals or chemical intermediates.

The charging stock which is to be converted according to the present invention comprises heavy high boiling oils containing catalyst contaminants or refractory constituents that render other methods of upgrading unattractive. Such materials as petroleum residua, coal tars, shale oils, asphalts, extracts, etc., are illustrative of suitable charging stocks.

According to this invention, a heavy oil, e. g., a vacuum residuum, is contacted in a fluidized solids fuels coking zone with particulate solids maintained at a coking temperature in the range of 850° to 1200° F. The oil, upon contact with the solids, undergoes vaporization and pyrolysis evolving relatively lighter hydrocarbon vapors and depositing residue on the solids. The time of contact is regulated so that only a part of the feed is converted to vapors. The solids along with the adhering remaining portion of the heavy oil are then withdrawn from the coking zone and mixed with additional high temperature particulate solids in a chemicals coking zone, preferably a transfer line zone, whereby the resulting mixture has a temperature in the range of 1200° to 1600° F. This results in the conversion of the remaining portions of the feed to light unsaturates and similar compounds suitable as chemical raw materials. After having entrained solids removed, the vaporous conversion products from the fuels and chemicals coking zones are separately recovered as products.

The solids separated from the chemical coking zone effluent are stripped and a major portion of the stripped solids is circulated to the fuels coking zone to maintain the coking temperature. The remainder is circulated through a heating zone wherein they are heated, preferably by partial combustion, to a temperature 100° to 900° F. above the temperature in the chemicals coking zone. The reheated solids are then returned to the chemicals coking zone.

It can be seen that this fluidized solids coking system provides, in essence, for the production of fuels at high solids-oil ratios or with low solids holding times in a fuels coking zone so that the oil undergoing treatment is not completely converted or cracked. The unconverted feed on the solids is then completely converted in a high temperature chemicals coking zone. The process utilizes a single inventory of circulating solids, and all of the heat for the process is supplied by a common heating system. The heating system comprises, preferably, a burner wherein a portion of the carbon-containing particles are partially combusted.

It is to be appreciated that this invention diverts to fuels production the lighter, high hydrogen containing, fraction of the feed and diverts the heavier, low hydrogen-containing, components to chemicals production. The present process is particularly adapted to handling a long residuum, i. e., a residuum containing a substantial proportion of constituents boiling below about 900° F. The fuels coking zone is utilized to secure vaporization of the lighter constituents of a long residuum, and the chemicals coking zone is utilized to completely convert the heavy low value ends of the residuum. The ease of controlling the fraction converted to fuels in the fuels coking zone results in a very flexible process.

The heat transferring particulate solids used in the practice of this invention comprise any finely divided, substantially catalytically inert, refractory solid such as pumice, kieselguhr, spent catalyst, sand, metal and refractory beds, etc. Particulate coke produced by the process is the preferred contact solid. As this is a fluidized solids process, the solids have, preferably, a size in the range of 40–500 microns, although in some instances the solids may vary considerably beyond these limits, e. g., from 0 to 1000 microns by screen analysis.

It is an object of this invention to devise a combination fuels and chemicals coking process which utilizes a single inventory of circulating coke and a common coke heating system.

The drawing, attached to and forming a part of this specification, will serve to illustrate one preferred embodiment of this invention. This drawing is for the purpose of illustration only and the invention is not to be limited thereto.

In brief compass, the objects of this invention are attained in the following manner: A charging stock is contacted in a fuels coking zone with a fluidized bed of high temperature particulate solids, preferably, finely divided coke. A relatively low solids residence time is maintained in the coking zone whereby only a portion of the charging stock is vaporized and converted to gasiform products. Solids along with adhering unconverted portions of the charging stock are removed from the fuels coking zone and transferred to a chemicals coking zone wherein they are admixed with additional amounts of high temperature solids to form a mixture having a temperature above 1200° F. The heated mixture is then passed through a transfer line chemicals coking zone and at this temperature the remaining portion of the charging stock is rapidly converted to coke and light hydrocarbons including a substantial proportion of unsaturates. The contact solids are then separated from the effluent from the chemicals coking zone. A major portion of the separated solids is transferred to the fuels coking zone to supply heat thereto; and the remainder of the separated solids is circulated through a heating zone and back to the chemicals coking zone.

Referring now to the attached drawing, the major items of equipment shown are a fluid bed fuels coker **10**, a transfer line chemicals coker **20** and a fluid bed burner vessel **30**. The feed to the process, e. g., a vacuum residuum, which may be suitably preheated to reduce the heat load of the system, is injected into fuels coker **10** via line **1**. The injected oil is admitted to the vessel at a multiplicity of points and an atomizing gas may be used to suitably disperse the oil on the fluidized solids.

The fuels coker **10** has maintained in it a fluid bed of particulate coke in a manner well known by the art. The fuels coking temperature may vary from about 850° to 1200° F. Lower temperatures below 1,000° F. are used when heavy distillates suitable as catalytic cracking feed stock are desired and somewhat higher temperatures above 1,000° F. are used when lighter distillates, e. g., naphthas are desired as the primary products. An inert fluidizing gas, preferably steam, is supplied to the base of vessel **10** by line **2**. Gas rates are adjusted to maintain fluidization velocities in the range of about 0.2 to 5 ft./sec.

A high solids to oil ratio, or conversely a low solids holding time, is utilized in the fuels coker such that only a portion of the injected feed is vaporized and converted. The amount of the feed converted in this zone is controlled primarily by the solids to oil ratio, but the coking temperature, fluidization gas rate, etc., may also be regulated to control the conversion. Generally, depending upon the nature of the feed, it is desired to convert approximately 30 to 80% of the feed in this zone to the products boiling below 1015° F.

The conversion products pass upwardly through the coking reactor to cyclone system **3** wherein entrained solids are removed from the vapors and returned to the fluid bed. This cyclone system may be external of reactor **10**. The vapors are then separated by conventional means, e. g., fractionation, to obtain the desired liquid distillate products. As illustrated, a superposed scrubber **4** is used to quench and remove from the vapors the heavy high boiling ends. The heavy ends condensed from the vapors by this scrubbing are conveniently recycled via line **5** to the coker to be retreated therein. A portion of these heavy ends are cooled in heat exchanger **6** and transferred to the top of scrubber **4** by line **7** to serve as the quench oil. The initial boiling point of the heavy ends condensed in this arrangement is preferably in the range of 950° to 1150° F. The quenched vapors are removed from the scrubber **4** by line **8** and are transferred to further conventional processing, not shown.

Solids along with the unconverted portions of the feed are transferred via line **9** to the chemicals coking zone **20**. At the inlet of the chemicals coking zone, the wet solids are met with additional amounts of high temperature solids supplied by line **22**, sufficient to raise the temperature of the mixture above 1200° F. The transfer line chemicals coker is preferably a vertically disposed, narrowly confined elongated conduit which may be suitably lined with refractory materials. A lift gas, preferably steam, although other gases such as light hydrocarbon gases may be used, is admitted to the base of the chemicals coker by line **11** in amounts sufficient to carry the suspension through the chemicals coker at velocities above 5 ft./sec.

At this high temperature, the liquid residue on the solids is rapidly converted to light unsaturates and similar compounds. To avoid undue thermal degradation of the conversion products, conversion times are held at a minimum. It is preferred to maintain the average vapor residence time of the conversion products before quenching in the range of 0.1 to 1.0 second. Stated somewhat differently, C_3 conversions, on a coke free basis, of the liquid residue transferred to the chemicals coker on the solids range from about 20 to 50 wt. percent. The solids in passing through the transfer line reactor are substantially completely dried with the carbonaceous residue deposited thereon forming coke which becomes a part of the solids. The effluent from the chemicals coker **20** is rapidly separated in a cyclonic separator **12**. The conversion products are removed from separator by line **13**. Preferably these products are quenched by a quench medium supplied by line **14** to below cracking temperatures, as they issue from the cyclonic separator. The quench medium used is preferably a heavy hydrocarbon oil and may be composed of the heavy ends removed in scrubber **4**. The quenched products in line **13** are then sent to conventional processing equipment to recover the desired chemicals and hydrocarbon fractions. Crystallization, fractionation, absorption, adsorption, etc., processes may be used to effect the desired separation.

The solids removed by separator **12** are transferred by line **15** to a stripping vessel wherein occluded hydrocarbons are removed from the solids. A stripping gas, e. g., steam, is admitted to the base of the stripping vessel **16** by line **17** in amounts sufficient to fluidize the solids therein. The gases are recovered overhead from the stripping vessel and transferred to the dilute solids phase in the fuels coker **10** by line **18**. A major portion of the solids in the stripping vessel **16** are transferred by line **19** to the fuels coker to supply heat thereto. A cooler, steam generator or heat exchanger **28**, is preferably used to partially cool the solids circulated to the fuels coker. This gives greater flexibility to the process in that the chemicals coker can be operated at higher temperatures and permits a higher solids/oil ratio to be used in the fuels coker without exceeding temperature limitations. Conveniently, steam can be generated in cooler **28** for use within the process.

The remainder of the solids in vessel **16** are transferred by line **21** to the burner vessel to be reheated. A lift gas, e. g., steam or air, is supplied to the contents of line **21** by line **23** to aid in the transfer of the solids to the burner vessel **30**. The method of circulating the contact solids used in the method of the present invention forms no part of this invention. Reference is made to co-pending application by Whiteley and Molstedt, Serial No. 439,702, to illustrate one method of circulating solids applicable to the present invention.

The means of supplying heat to the process also forms no part of the present invention. As shown, a fluid bed burner vessel is used to partially combust the carbon-containing solids transferred thereto. Air or other free oxygen-containing gas is admitted to the base of the burner vessel **30** by line **24** in amounts sufficient to fluidize the solids therein and to support a partial combustion of the solids. By this means, the temperature of the solids is raised to a temperature 100° to 900° F. above the chemicals coking temperature. Entrained solids are removed from the flue gases by a cyclone separator system **25** located in the dilute solids suspension phase above the fluid bed. The flue gases are then vented by line **26**. Normally an excess of coke is produced by the process and this excess may be removed by line **27**. The reheated coke is transferred to the chemicals coker **20** by line **22** as previously described.

Other means of supplying heated solid particles to the coking process can, of course, be used. Besides the fluid bed burner illustrated, gravitating bed burners or transfer line burners may be used to accomplish the partial combustion. Other direct or indirect heat exchange means may be used if desired, such as shot heating systems, and, further, extraneous liquid or gaseous fuels may be preferentialy combusted in the burner to heat the solid particles.

The range of operating conditions applicable to the process illustrated in the drawing are summarized in Table I. Table I also presents a specific example of operating conditions. Table II presents a specific example of the products obtainable from the charging stock indicated when a process is operated in accordance with the example of Table I.

TABLE I

	Range	Example
Contact Solid		Coke.
Particle Size, Microns	0 to 1,000	40 to 500 microns.
Median Particle Size, Microns		250 microns.
Fluid Bed Fuels Coker:		
Pressure @ vapor outlet, p. s. i. g.	0 to 400	6.
Coking temperature, ° F	850 to 1,200	950.
1,015° F. Conversion,[1] percent	40 to 90	58.
Temperature fresh solids, ° F	1,000 to 1,600	1,300.
Coke/oil ratio	1 to 20	6.
Average solids, residence time, min.	1 to 10	2.
Fluidizing steam rate, wt. percent fresh feed.	2 to 50	5.
Bed density, lbs./C. F		40.
Transfer line chemicals coker:		
Pressure @ outlet, p. s. i	0 to 400	6.
Avg. temperature, ° F	1,200 to 1,600	1,300.
Reheated coke/wet coke from fuels coker ratio.	0.1 to 10	1.
Temperature of reheated coke	1,400 to 2,000	1,650.
Lift gas rate, C. F./lb. wet coke	0.05 to 1	0.48.
Solids loading, lbs./C. F	1 to 20	4.
Coke throughput, lbs./Min./ft.^{2}	1,000 to 20,000	10,000.
Solids velocity, ft./sec	Above 5	20.
Average vapor residence time before quenching, sec.	0.1 to 10	1.
C_3 conversion,[2] percent	10 to 50	30.
Fluid Bed Burner:		
Temperature, ° F	1,400 to 2,000	1,650.
Bed density, lbs./C. F	25 to 50	40.

[1] 1,015° F. conversion is defined as 100 vol. percent fresh feed minus products boiling above 1,015° F. less coke.

[2] C_3 conversion is defined as wt. percent of products having three or less carbon atoms divided by 100 wt. percent fresh feed, on a coke free basis.

TABLE II

Feed: South Louisiana long residuum

17.7 API gravity
4.8 wt. percent Conradson carbon
850° F. initial boiling point
0.1 wt. percent ash
1.51 H/C atomic ratio

Products: percent on fresh feed

CHEMICALS COKER

Hydrogen	wt. percent	0.1
Methane	wt. percent	1.3
Ethane	wt. percent	0.5
Ethylene	wt. percent	1.8
Propane	wt. percent	1.0
Propylene	wt. percent	1.6
C_4 Hydrocarbons	vol. percent	2.5
Benzene	wt. percent	0.6
Aromatic tar	wt. percent	5

FUELS COKER

C_3—	wt. percent	4.0
C_4 Hydrocarbons	vol. percent	1.5
C_5—430° F., naptha	vol. percent	10.5
430°-1015° F. gas oil	vol. percent	63.5
Gross coke make	wt. percent	5.3

NOTE.—All 1015° F.+material from fuels coker effluent is recycled to extinction.

Numerous variations of this invention will occur to those skilled in the art. It is to be appreciated that in certain applications either a transfer line reactor zone or a fluid bed fuels coking zone may be used to accomplish either the initial low temperature conversion of the feed or the high temperature conversion of the remaining portions of the feed. As indicated, however, a fluid bed operation is preferred for the fuels coking step and, because of the short contact times required in the chemicals coking zone, a transfer line reactor zone is preferred for this step. As an example of another variation, instead of stripping all of the solids in line **15**, only the portion transferred to the burner vessel need be stripped.

Having described the invention, what is sought to be protected by Letters Patent is succinctly set forth in the following claims.

What is claimed is:

1. A fluidized solids petroleum residua coking process for converting charge stock to fuels products and chemical unsaturates which comprises, in combination, coking a charging stock in a fluid bed fuels coking zone while maintaining a relatively low solids residence time whereby only a portion of the charging stock is converted to gasiform products, withdrawing solids and unconverted charging stock from the fluid bed, heating the withdrawn portion to a temperature above 1200° F. by adding additional high temperature solids, passing the heated portion through a transfer line reactor to convert the remaining portions of said charging stock to coke and light unsaturates while maintaining an average vapor residence time of less than 10 seconds in said transfer line reactor, and separating and recovering the conversion products from each zone from the contact solids therein.

2. A hydrocarbon conversion process which comprises injecting a heavy hydrocarbon oil into a fuels coking zone containing a fluidized bed of particulate coke maintained at a fuels coking temperature in the range of 850° to 1200° F. to produce relatively lighter normally liquid conversion products while maintaining an average solids residence time in said fuels coking zone within the range of 1 to 10 minutes whereby a 1015° F. + conversion in the range of 40 to 90% is obtained, introducing heated coke particles into said fuels coking zone at a solids/oil ratio in the range of 1 to 10, removing entrained solids from and recovering said conversion products, withdrawing particulate coke along with the liquid residue of said charging stock and heating the withdrawn coke to a chemicals coking temperature in the range of 1200° to 1600° F. by mixing said withdrawn coke with 0.1 to 10 parts of additional coke per part of withdrawn coke having a temperature 100° to 900° F. above the temperature of said withdrawn coke, passing the resulting mixture through a transfer line chemicals coke at velocities above 5 feet/sec., whereby the remaining, heavier portion of said charging stock is converted to light hydrocarbon gases and coke, the average vapor residence time before quenching in said transfer line chemicals coker being under 10 secs., separating coke from said light hydrocarbon gases and recovering the gases as product, stripping the coke so separated, partially cooling and returning a major portion of the coke so stripped to said fuels coking zone as said heated coke particles, circulating the remaining portion of the stripped coke to a heating zone wherein the temperature of the coke is raised 100° to 900° F. above said chemicals coking temperature by partial combustion, and returning the reheated coke to said chemicals coking zone.

3. A combination fluid coking process for producing distillate fuels and chemical raw materials which comprises coking a petroleum residual oil in a fuels coker containing a fluid bed coking zone with a low solids holding time whereby only a portion of the residual oil is converted and the remainder is deposited on the solids, passing solids from said fluid bed coking zone to a transfer line chemicals coker, mixing additional hot solids with the solids in the chemicals coker to raise the temperature therein above 1200° F., passing the mixture through said chemicals coker for a relatively short reaction period whereby light unsaturates are produced, separating solids from the effluent from said chemicals coker, passing a major portion of the solids so separated to said fuels coking zone to supply heat thereto, and circulating the remainder of the separated solids to a heating zone and back to said chemicals coker.

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