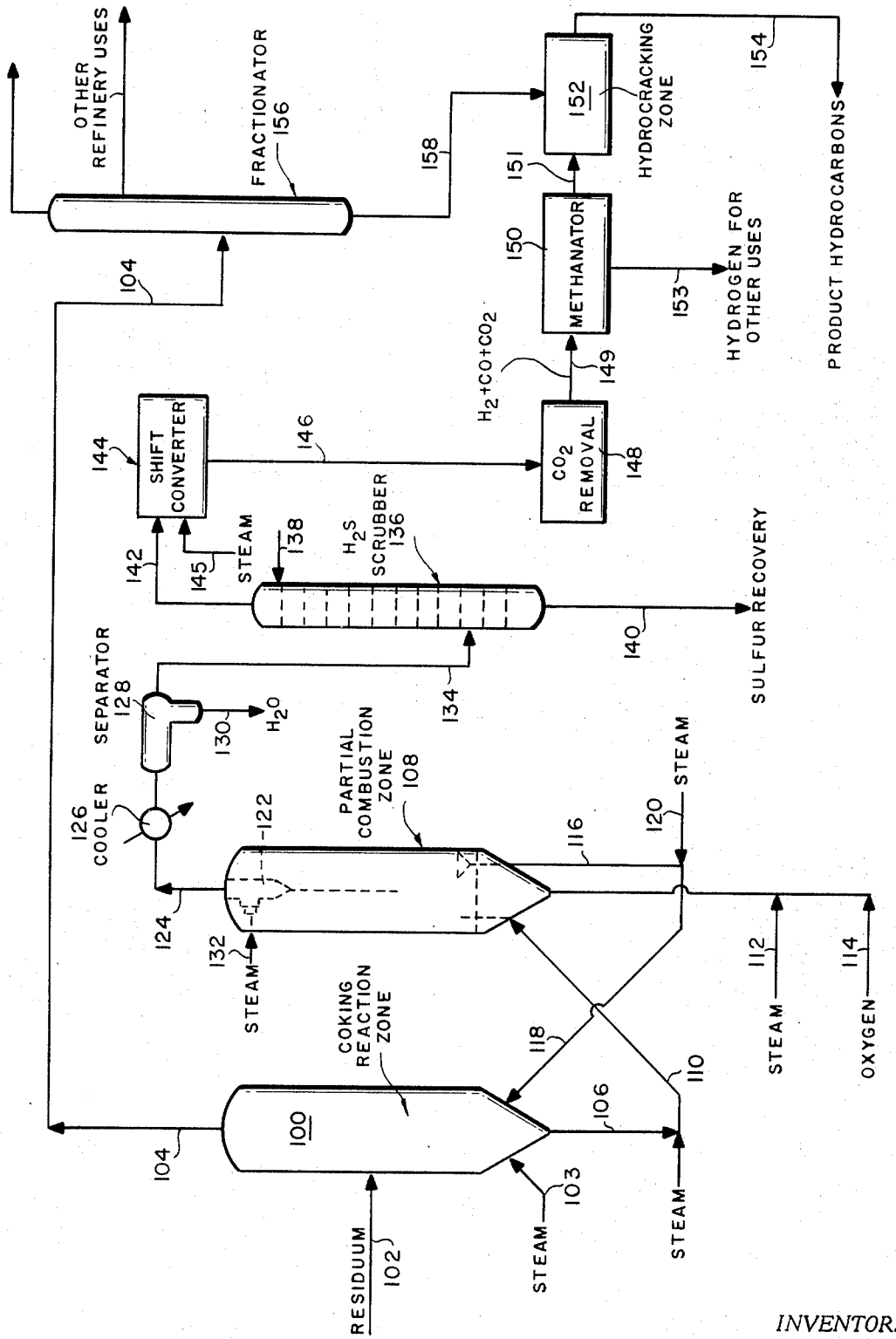
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PROCESS FOR PRODUCING LIGHT PRODUCTS FROM HEAVY HYDROCARBONS

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# PROCESS FOR PRODUCING LIGHT PRODUCTS FROM HEAVY HYDROCARBONS

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## ABSTRACT OF THE DISCLOSURE

A heavy hydrocarbon stream is converted in a high-temperature, high pressure fluidized coker into a distillable, lower-boiling hydrocarbon product oil while producing a coke product. The coke product is converted in a high-pressure, high-temperature, partial combustion reactor into carbon monoxide, by reaction with steam and a small amount of substantially pure oxygen. The carbon monoxide is converted into carbon dioxide in a shift reactor. The hydrogen produced in the water-gas reactor and the shift reactor is preferably used to hydrocrack the lower-boiling hydro-carbon oil product from the coker, or may be used for other purposes such as hydrofining, etc.

This application is a continuation of S.N. 693,303, now abandoned.

## BACKGROUND OF THE INVENTION

Heavy hydrocarbons such as residuum (particularly when containing appreciable amounts of sulfur) can best be cracked into light products by thermal (coking) processes. Such heavy hydrocarbons have been converted into lower-boiling products in fluid cokers such as that disclosed in Jones et al. Pat. 2,895,904 (especially FIG. 2). These fluid cokers have been operated at low pressures, and the coking temperature has been maintained by burning from 10 to 30% of the coke product, by combustion with air in a separate burning zone (such as zone **64** of the Jones et al. patent). The product coke is removed from the coker in amounts corresponding to the difference between the coke being formed from fresh feed and coke being consumed to support the coking temperature. Currently, there is a very limited market for sulfur-containing coke such as that produced in a fluid coker from a "sour" residuum, and only a limited market even for low-sulfur fluid coke which is produced from "sweet" residua. The resulting excess supply of coke gives rise to a disposal problem; in at least one case the unwanted coke was accumulated in a pile for a number of years before the resulting "mountain" could be sold. Attempts to burn the coke in the combustion zone have also proven to be unsatisfactory, since the heat generated in such a system is far in excess of that required for the coking reaction. By the present invention, this coke is used to produce hydrogen, thus allowing the desirable thermal conversion process to be used for initial conversion of the heavy hydrocarbon feed, and the hydrogen is then available for use in a subsequent hydrogenation step for hydrofining or hydrocracking all or selected portions of the coker gas oil product (or for use in hydrotreating other feedstocks if desired).

Hydrogen is used in many refinery operations for hydrocracking, olefin and aromatic hydrocarbon conversion, or sulfur and/or nitrogen removal. It has been suggested that hydrogen can be produced by the reaction of coke with steam at elevated temperatures, either with or without the addition of oxygen to the water-gas reaction zone. This is shown, for example, in FIG. 1 of the Nelson et al. patent, U.S. 2,729,552, where coke is contacted at 400–500 p.s.i.g. and 1800–1900° F. with steam and oxygen. The prior art has not, however, recognized the unique advantages of the present invention, wherein the coker and partial combustion zone are used to produce CO for later conversion into hydrogen.



By the present invention, the temperature and pressure of the coking step are raised so as to be compatible with a high-temperature, high-pressure partial combustion reaction zone, and high purity oxygen is used in the partial combustion reaction zone to promote the formation of carbon monoxide for later use in producing hydrogen in the shift reaction. The use of high pressures and pure oxygen make it economically feasible to produce hydrogen from residuum, by reducing the size (and cost) of the conversion vessels. Surprisingly, the use of pure oxygen for combustion to provide heat for the coker does not increase the cost of operations by an amount sufficient to offset the investment savings, because the combustion is incomplete and the carbon monoxide is used to produce hydrogen. In its most specific aspect, the present invention provides a balanced, self-contained process for producing light products from heavy feedstocks, generating the hydrogen required for hydrocracking without the need for an external hydrogen supply.

## SUMMARY OF THE INVENTION

The present invention utilizes a partial combustion reactor to perform two functions: (1) to provide heat for operation of the fluid coker which itself supplies coke to the partial combustion reactor and (2) to convert coke, oxygen and steam into carbon monoxide and hydrogen, with a minimal production of carbon dioxide and with substantially no net coke make for the system. It has been found that the small amount of ash which is formed is taken off overhead with the gas product and can easily be separated therefrom for disposal. It has also been found that the fluid coker can be easily operated at temperatures and pressures high enough to meet the requirements of the system.

The coker is operated to treat a heavy hydrocarbon oil such as residuum at a temperature of 600 to 1200° F. and a pressure from 150 to 1500 p.s.i.g. (preferably 900° F. at 200 p.s.i.g.) and the coke product is substantially all converted into gaseous products (CO, $CO_2$ and $H_2$) by contact with steam and substantially pure oxygen in a partial combustion reactor at a temperature of 1200 to 2400° F. and a pressure of 100 to 2000 p.s.i.g. (preferably 1800° F. and 200 p.s.i.g.). In the partial combustion reactor, the oxygen/steam mol ratio is from 0.05 to 0.5 and the steam partial pressure is from 1 to 250 p.s.i. (preferably a ratio of 0.15 and a partial pressure of 20 p.s.i.).

The carbon monoxide content of the gaseous product of partial combustion is converted into carbon dioxide by reaction with steam in a shift converter, thus producing more hydrogen. A purified hydrogen stream is obtained by removal of $H_2S$ and $CO_2$, and conversion of residual CO (and $CO_2$) into methane. The resultant hydrogen stream is useful for many refinery purposes, but is preferably used to hydrocrack the coker gas oil which is produced in the first step.

## BRIEF DESCRIPTION OF THE DRAWING

The single figure in the drawing is a schematic representation of the present invention, set out as a flow diagram.

## DESCRIPTION OF THE PREFERRED EMBODIMENT

In the present invention, the coker and partial combustion reactor are mutually dependent; that is, the coker

depends upon the partial combustion reactor for a large amount of its heat input, and the partial combustion reactor depends on the coker for its carbonaceous feed. The hydrocracking reactor is dependent on both, since the coker gas oil is hydrocracked with hydrogen produced directly and indirectly by action of the partial combustion reactor. Each of these main areas, as well as intervening steps, is treated separately below.

Coker: The coker converts a heavy, hydrocarbonaceous liquid feedstock (such as petroleum residuum) into lighter products. The reaction is thermal and is carried out in a fluidized bed as is generally described in the Jones et al. patent, but at higher pressures so as to be in pressure balance with the partial combustion reactor. Fluidization is accomplished by the introduction of superheated steam, and is assisted by the formation of lighter products by pyrolysis of the feedstock.

Suitable heavy hydrocarbon feedstocks are petroleum pitch, crude residua, topped crude, etc. Coal extracts or a slurry of coal or char in an oil slurry may be used as a feedstock if a system for ash removal is employed (such as that shown in our copending application based on CSO 67.3 and entitled "Ash Removal in Gasification of Carbonaceous Solids," Ser. No. 691,330 (now U.S. Pat. 3,440,177, issued Apr. 22, 1969).) An exemplary feedstock is a residual oil having the following characteristics:

TABLE I.—CRUDE RESIDUUM

API gravity: 9.0°
Conradson carbon: 20 wt. percent
Boiling range: 1000° F.+, vapor temperature

Such a residuum is obtained by the vacuum distillation of topped crude oils, such as a West Texas sour crude. It contains a comparatively large amount of combined sulfur and is therefore impossible to crack with sulfur-sensitive catalysts. The high Conradson carbon content also makes it difficult to treat with a sulfur-insensitive catalyst due to deactivation of the catalyst by carbon laydown. Trace quantities of contaminant metals such as nickel, vanadium, etc. make the residuum an unsuitable feedstock for fluidized bed catalytic cracking. Thus, the thermal cracking process which is carried out in a fluid coker is the process most suited for handling this difficulty, since there is no catalyst to be deactivated or contaminated, and the benefits of a fluidized bed can be obtained.

The fluid coker is preferably operated under conditions chosen to (1) minimize the formation of aromatic and olefinic hydrocarbons and (2) produce a coke product under pressures suitable for transferring the coke to the partial combustion reaction zone. The first object is attained by maintaining the temperature below 1200° F., while the second object is attained by operating at pressures slightly higher than the pressure in the partial combustion reactor. Coke make is about 25 weight percent of the feed, the remainder of the products being liquids and gases. An exemplary product inspection is shown in Table II.

TABLE II.—PRODUCTS OF COKING ZONE

| | Vol. percent | Wt. percent |
|---|---|---|
| Gases, $C_3$ and lighter | | 9.0 |
| Liquids | | 66.0 |
| Total $C_4$'s | 4 | |
| Naphtha ($C_5$–430° F.) | 25 | |
| Gas oil (430–1,015° F.) | 71 | |
| Total | 100.0 | |
| Coke | | 25.0 |
| Ash, wt. percent | 1 | |
| Sulfur, wt. percent | 1–5 | |
| Carbon plus hydrocarbons, wt. percent | 94–99 | |
| Total | | 100.0 |

Preferably, only the gas oil is later hydrocarcked although the naphtha may also be hydrocarcked, separately or in admixture with the gas oil.

Operating conditions in the coker are summarized below in Table III.

TABLE III.—COKER OPERATING CONDITIONS

| | Minimum | Maximum | Preferred |
|---|---|---|---|
| Temperature, ° F | 600 | 1,200 | 900 |
| Pressure, p.s.i.g | 150 | 2,000 | 200 |
| Steam, wt. percent of liquid feed | 0.5 | 10 | 2 |
| Feed rate, bbl. liquid/# coke [1]/hr. | 0.3 | 5.0 | 0.5–1.0 |
| Fluidizing gas velocity, ft./sec | 0.5 | 3.0 | 2.5 |
| Bed density, #/cu. ft | 10 | 60 | 40 |

[1] Coke is fluidized bed within the coker.

The steam which is used for fluidizing the coke particles is introduced near the bottom of the coker and serves also to strip occluded hydrocarbons from the surface of the coke being transferred into the water-gas reactor. Substantially all of the net coke make is consumed in the water-gas reactor, but a circulating stream of coke is maintained for purposes of heat transfer. Since the coking reaction is endothermic, heat is transferred from the partial combustion reaction zone into the coker by means of coke circulation. This circulation amounts to 2 to 10 pounds of coke per pound of liquid feed, preferably about 3 pounds. Preheating the feed is desirable to reduce the amount of circulation and increase hydrogen yield.

Partial combustion zone: In the partial combustion zone, the coke is heated by combustion in an oxygen-poor atmosphere to a temperature of 1200° F. to 2400° By diluting the oxygen with steam (rather than with nitrogen, as in air) and maintaining high temperatures (e.g., 1880° F.+) a second reaction is also accomplished: coke and steam. These two reactions are shown below.

$$2C+O_2 \rightarrow 2CO+58{,}000 \text{ cal.} \quad (1)$$

$$C+H_2O \rightarrow CO+H_2—30{,}000 \text{ cal.} \quad (2)$$

Thus, it is seen that the exothermic oxidation reaction produces enough energy from the combustion of one mol of carbon to support the reaction of another mol of carbon and water, both reactions producing CO. However, the *coking* reaction is endothermic, and a certain proportion (about one-half) of the released energy is transferred (by coke circulation) to the coking reactor to support that reaction. About one-half of the energy is thus available to support the water-gas reaction. By controlling the amount of oxygen present, and by using steam to control the temperature (i.e., by controlling the rate of reaction), a product gas rich in CO can be obtained. The CO can then be converted to $CO_2$ by reaction with steam in a subsequent shift reaciton step, yielding 1 mol of hydrogen for each mol of CO reacted.

The conditions in the partial combustion/water-gas reaction zone are summarized in the following able.

TABLE IV.—PARTIAL COMBUSTION REACTOR OPERATION CONDITIONS

| | Minimum | Maximum | Preferred |
|---|---|---|---|
| Temperature, ° F | 1,200 | 2,400 | 1,800 |
| Pressure, p.s.i.g | 150 | 2,000 | 200 |
| Steam pp., p.s.i.a | 1 | 250 | 20 |
| Oxygen/steam mol ratio | 0.05 | 0.5 | 0.15 |
| Coke recirculation lb./lb. liquid feed | 2 | 10 | 3 |

A temperature of 1800° F. is preferred in order to obtain the benefits of the water-gas reaction $C+H_2O \rightarrow CO+H_2$ as well as the partial combustion reaction $2C+O_22 \rightarrow CO$. At lower temperatures the water-gas reaction does not occur to a substantial extent, but the partial combustion reaction is effective at temperatures as low as 1200° F. The oxygen stream is admitted in a stream at least 98%, but preferably at least 99.5% (by volume), pure. Such an oxygen stream is obtained by liquefaction and distillation of air, and is available under suitable pressures (e.g., 100 to 400 p.s.i.g.) so that it need not be recompressed at the unit limits of the partial combustion reactor. Thus, the expensive air blowers of the prior art

may be omitted entirely, as may be the gas compressors normally required for light hydrocarbons from the coker reactor, since the coker is also operated at high pressures. As has been stated above, the use of higher pressures and the elimination of nitrogen allow the reactors to be reduced in size, thus providing even more economy in plant investment.

The effluent from the water-gas reaction zone will include unreacted steam, carbon monoxide, carbon dioxide, hydrogen, and trace contaminants such as hydrogen sulfide and nitrogen. Exemplary ranges of the constitutents are given in the table below.

TABLE V.—CONSTITUENTS OF WATER GAS PRODUCT, VOL. PERCENT

| | Minimum | Maximum | Preferred |
|---|---|---|---|
| Product gases, dry basis: | | | |
| CO | 30 | 60 | 43 |
| $CO_2$ | 0 | 20 | 5 |
| $H_2$ | 20 | 60 | 47 |
| $H_2S$ | 0 | 10 | 3 |
| $N_2$ | 0 | 5 | 2 |

Thus, it is seen that the partial combustion reactor product is preponderantly made up of carbon monoxide and hydrogen, with only small amounts of $CO_2$ being produced. The CO is later converted, on virtually a mol-per-mol basis, into $CO_2$ while yielding hydrogen as a product. Before this is accomplished in the shift conversion reactor, however, it may be desirable to remove the hydrogen sulfide contaminant, so as to avoid poisoning of the shift catalyst.

Hydrogen sulfide removal: Particularly when the catalyst in the shift converter is sulfur sensitive, it is desirable to treat the carbon monoxide-rich gas to effect the removal of hydrogen sulfide therefrom. The product gas is preferably first passed through a condenser and separator to remove substantially all of the unreacted steam, to avoid undue dilution of the $H_2S$ solvent. The "dry" gas (i.e., with most of the steam removed) is then contacted with a suitable solvent in a liquid-gas contacting apparatus such as a packed column (Beryl Saddles or Raschig rings are suitable). Solvents such as ethanolamine, methyl ethyl amine, potassium carbonate, sodium carbonate, sodium hydroxide (polysulfide), etc., can be used at a temperature from about 100–400° F. The ratio of solvent circulated per m.s.c.f. of gas feed may be from 100 to 1000 pounds per m.s.c.f. Sulfur may be recovered from the solvent, e.g., by the Claus process.

Shift conversion: In the shift conversion zone, carbon monoxide is rected with steam in the presence of a suitable catalyst to produce carbon dioxide and hydrogen. This well-known process is carried out in the presence of suitable catalysts, most of which are sulfur-sensitive. (A sulfur-insensitive cobalt-molybdate catalyst is described and claimed in a copending application Ser. No. 687,681 (now abandoned) by Glenn A. Stankis based upon BPRL 67.29, and entitled "Production of Hydrogen.") The reaction is represented as

$$CO+H_2O \rightleftarrows CO_2+H_2$$

Exemplary of sulfur-sensitive catalysts are iron oxide, iron sulfide, copper/zinc supported on alumina, etc. Use of the catalyst allows reduction of the temperature to favor production of $CO_2$: to a range from 500° F. to 900° F. Carbon dioxide is removed from the product by any of a number of well-known expedients, such as adsorption on solids or absorption by liquids. Suitable solids are alkaline earth oxides, such as the oxides of calcium, barium or strontium. Calcium oxide (lime) is a cheap and readily available material. See U.S. Pats. 3,188,179 and 3,108,857. Residual CO and $CO_2$ may be undesirable and are preferably converted to methane by reaction with hydrogen in a methanation zone in contact with a suitable catalyst, all as is well known in the art.

The CO and $CO_2$ having been removed, the high-purity hydrogen stream can be used for any purpose. Preferably, however, it is used to provide hydrogen in the hydrotreatment (e.g., hydrocracking) of coker gas oil produced in the coking zone. A molecular sieve-type catalyst may be used in the hydrocracking zone, and the reaction is carried out at high pressures (e.g., 2000 p.s.i.g.) and temperatures (e.g., 700° F.), all as is well known in the art.

Schematic flow diagram: The process of the present invention can be seen as a whole by advertence to the drawing wherein it is seen that a heavy oil, such as residuum, is introduced into a coking reaction zone **100** by way of line **102**, for conversion into a distillable product which is removed by way of line **104** to a fractionator **156**, and into a coke product which is removed by way of line **106**. The coke product is transferred into a partial combustion zone **108**, preferably by means of a differential pressure and fluidation steam stream which transports the carbon through line **110** into the lower portion of the partial combustion zone **108**. In the partial combustion zone, the coke is contacted with steam which is introduced by way of line **112** and oxygen introduced by way of line **114**, as well as the steam in the transporting stream.

From the partial combustion zine, a recycle coke stream is removed by way of line **116**. This recycle coke stream may be carried into the reaction zone **100** through line **118** by means of differential pressure and fluidation steam or an inert gas stream introduced by way of line **120**.

The unreacted steam and gaseous products from the partial combustion zone are removed therefrom through an internal or external cyclone separator **122**, and are passed through line **124** into a cooler or steam generator **126** and separator **128**, for the condensation and separation of water which is removed by way of line **130**. If desired, steam may be introduced into the inlet into the cyclone separators by means of line **132**. This improves the operation of the cyclone separators and minimizes metallurgical problems associated with the high temperatures in the partial combustion zone.

The water-free product gas containing carbon monoxide, hydrogen sulfide, and some $CO_2$ is passed by way of line **134** preferably into a hydrogen sulfide scrubber **136**. In the hydrogen sulfide scrubber, the gas stream is contacted with a solvent (such as potassium carbonate) introduced by way of line **138** and removed by way of line **140**, which serves to absorb the hydrogen sulfide.

The hydrogen sulfide-free gaseous product, now consisting essentially of carbon monoxide, hydrogen, and some carbon dioxide, is passed by way of line **142** into a shift converter **144**, wherein the gas is contacted with steam introduced by way of line **145** under conditions chosen to convert the carbon monoxide into carbon dioxide. The catalyst used in this zone may be sulfur sensitive (iron oxide or iron sulfide, for example). If a sulfur resistant catalyst is used, the hydrogen sulfide removal step may be placed downstream of the shift converter rather than upstream. In such a case, the cooler **126** would reduce the gas temperature to a level suitable for shift conversion **144**, and a conventional high temperature filter (or filters) would be placed between generator **126** and shift converter **144** to remove any particulate matter not removed in the cyclones.

From the shift converter, a gaseous product is passed by way of line **146** into a carbon dioxide removal zone **148**. In the carbon dioxide removal zone, the gas is scrubbed with a solvent such as potassium carbonate or methanol, to absorb the carbon dioxide, or it is contacted with a solid such as calcium hydroxide or calcium carbonate to effect the removal. From the $CO_2$ removal zone, a hydrogen-enriched stream is removed by way of line **149** for introduction into a methanator **150** to remove the last traces of CO and $CO_2$ and thence to other uses **153** or (preferably) to the hydrocracking zone **152** via line **151**, where it is contacted with at least a portion of the distillable product from the fractionator **156** via line **158**, which is hydrocracked in the well-known manner. A product hydrocarbon stream is obtained by way of line

154, which may be fractionated into the desirable boiling ranges and post-treated as is needed.

Having described our invention, we claim:

1. A process for converting a heavy hydrocarbon liquid boiling above 1000° F. into lighter products which comprises:

(a) in a fluidized bed coking zone, coking said heavy hydrocarbon liquid

at a temperature from 600–1200° F.,
at a pressure from 150 to 1500 p.s.i.g., and
at a feed rate from 0.3 to 5.0 barrels of liquid feed per hour per pound of fluidized coke within the reactor, whereby a distillable liquid product and a coke product are obtained;

(b) continuously withdrawing only one portion of the fluidized coke from said coking zone and introducing all of that portion into a fluidized bed partial combustion zone,

(c) in said partial combustion zone, reacting said coke in a fluidized bed with steam and 95%+ pure oxygen in the absence of air

at a temperature from 12 to 2400° F.,
at a pressure from 150 to 2000 p.s.i.g.,
at a steam partial pressure from 1 to 250 p.s.i.a., and
at an oxygen/steam mol ratio from 0.05 to 0.5,

said conditions being correlated to minimize the production of carbon dioxide and maximize the production of carbon monoxide, whereby a product gas rich in carbon monoxide and hydrogen is obtained, and

(d) continuously removing only one portion of said fluidized bed from the partial combustion zone and recycling all of that portion into the coking zone, in quantities sufficient to provide the heat necessary to support the coking reaction,

(e) all of the conditions in both the coking zone and in the partial combustion zone being correlated so as to have substantially no net production of unconsumed coke.

2. A method in accordance with claim 1 wherein the conditions in the coking zone are:

Temperature: about 900° F.
Pressure: about 200 p.s.i.g.
Steam rate: about 2 lbs. per hundred lbs. of feed
Feed rate: about 0.5 to 1.0 barrel per hour per pound of coke in the fluidized bed,

and wherein the conditions in the partial combustion zone are:

Temperature: about 1800° F.
Pressure: about 200 p.s.i.g.
Steam partial pressure: about 20 p.s.i.a.
Oxygen/steam mol ratio: about 0.5.

3. A method in accordance with claim 1 further comprising the steps of:

(f) separating unreacted steam from the partial combustion zone product gas to obtain a dry gas;

(g) contacting the dry gas with a suitable material for removing sulfur therefrom and to obtain a sulfur-free gas;

(h) contacting the sulfur-free gas with steam and a shift-reaction catalyst, whereby the carbon monoxide is predominantly converted into carbon dioxide with the production of additional hydrogen; and

(i) separating the unreacted steam and carbon dioxide from the hydrogen product,

whereby an enriched hydrogen stream is obtained.

4. A process of converting a heavy hydrocarbon liquid boiling above 1000° F. into lighter products which comprises:

(a) in a fluidized bed coking zone, coking said heavy hydrocarbon liquid



at a temperature from 600 to 1200° F.,
at a pressure from 150 to 1500 p.s.i.g., and
at a feed rate from 0.3 to 5.0 barrels of liquid feed per hour per pound of fluidized coke within the reactor,

whereby a distillable liquid product and a coke product are obtained;

(b) continuously withdrawing only one portion of the fluidized coke from said coking zone and introducing all of that portion into a fluidized bed partial combustion zone,

(c) in said partial combustion zone, reacting said coke in a fluidized bed with steam and 95%+ pure oxygen

at a temperature from 1200 to 2400° F.,
at a pressure from 150 to 2000 p.s.i.g.,
at a steam partial pressure from 1 to 250 p.s.i.a., and
at an oxygen/steam mol ratio from 0.05 to 0.5,

said conditions being correlated to minimize the production of carbon dioxide and maximize the production of carbon monoxide, whereby a product gas rich in carbon monoxide and hydrogen is obtained;

(d) continuously recycling a portion of said fluidized bed from the partial combustion zone into the coking zone in quantities sufficient to provide the heat necessary to support the coking reaction;

(e) contacting said carbon monoxide and hydrogen-rich product gas with a shift catalyst under reaction conditions whereby the carbon monoxide is converted into carbon dioxide by reaction with steam;

(f) separating the carbon dioxide from the products of the shift reaction, leaving a hydrogen-rich stream as a product;

(g) reacting at least a portion of the distillable liquid product of step (a) with at least a portion of the hydrogen-rich product stream under hydrocracking conditions,

whereby a light hydrocarbon product is obtained.

5. A method in accordance with claim 4 further comprising the steps of removing sulfur from the gaseous product of step (c) before it is contacted with the shift reaction catalyst.

6. A method in accordance with claim 5 wherein the conditions in the coking zone are:

Temperature: about 900° F.
Pressure: about 200 p.s.i.g.
Steam rate: about 2 lbs. per hundred lbs. of feed
Feed rate: about 0.5 to 1.0 barrel per hour per pound of coke in the fluidized bed,

and wherein the conditions in the water-gas reaction zone are:

Temperature: about 1800° F.
Pressure: about 200 p.s.i.g.
Steam partial pressure: about 20 p.s.i.a.
Oxygen/steam mol ratio: about 0.5.


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