FIG. 2a

HYDROGEN STRIPPING AND REFORMING SECTION
FIG. 2b

DISTILLATION, CRACKING
AND CONTACT COKEING
SECTION

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The thermal cracking of large hydrocarbon molecules into smaller and lower boiling point compounds, is fundamental to the refining of petroleum. Unfortunately, while the cracking of large paraffin molecules into desirable smaller molecules is readily accomplished, there is a number of undesirable side reactions which complicate the usual process. Chief among these undesirable side reactions are the formation of heavy polymers and of light permanent gases. Thus, cracking is normally a process of both decomposition and polymerization. However, if the time of residence at cracking temperature can be made very short, decomposition processes predominate and polymerization is minimized and the resulting product exhibits a narrower and more uniform range of molecular weights. It is an object of this invention to provide a unique system which the residence time at cracking temperature can be controlled and made short as desired.

Known sophisticated cracking processes aim at producing a maximum percentage of compounds in the molecular weight range of 100 (gasoline) and a minimum of both light gases and heavy polymerized compounds. Most improvements in kinetic cracking incorporate some means for controlling the time at which the feedstock is subjected to cracking temperatures. Many processes which cannot achieve ultra-short residence times at very high temperatures, must include a catalyst which favors the production of a preponderance of desirable molecules and absorbs whatever heavy polymer is formed. At very high vapor phase cracking temperatures, that is, above 1200° F., the rate of decomposition is rapid (doubling once for every increase of about 30-70° F.) and the time of retention at higher temperatures, for optimum gasoline yield, must necessarily be measured in tenths or even hundreds of a second. Furthermore, the effect of specific cracking catalysts becomes less and less important as the temperature is raised and the residence time is shortened. This invention provides a unique arrangement for cracking petroleum without the necessity of catalysts in a reaction vessel and in which the petroleum is directly contacted with a very hot solid material for a controlled and preferably very short residence time.

The refining of high-sulphur and/or low-gravity crude petroleums as presently practiced constitutes a cumbersome, costly, unprofitable process incorporating a sequence of compromise functions dictated by prevailing market conditions and enormously complicated by the economic necessity of converting into salable products various incidental side streams of unsaturated and complex hydrocarbons which are inadvertently produced by the conventional refining system.

Moreover, in the United States, today, the combustion of sulphurous petroleum products results in the very serious pollution of the atmosphere. While modern refining practices largely remove sulphur from gasoline and the lighter fuel oils, the sulphur is usually concentrated in the residua which are eventually burned. The present state of the art of petroleum refining permits to be dumped into the atmosphere each year 3,000,000 to 4,000,000 tons of sulphur in various chemical combinations, some of which are highly toxic to human beings and all of which cause eye irritation, damage to plants and very serious metallic corrosion of exposed structures. It is an object of this invention to eliminate practically all of the sulphur from the distillate and cracked products before fractionation into the final products and recycle stock. Because of the relative simplicity afforded this system for the controlled decomposition of paraffins to olefins and of napthenes to aromatics, desulfurization of the primary vapor streams can be complete and performed...
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without regard to the saturation of whatever olefines and aromatics which are initially formed. It is a further object of this invention to provide a unique petroleum refining scheme in which no residual oil is produced, thus allowing the production of high grade gasoline from low grade crude and eliminating the necessity for marketing heavy residual oils with a high sulphur content. Since no residual oils are generated by the process a greater yield of high value products is produced and the overall profitability of petroleum refining is substantially increased.

The multivapor petrofiner of this invention incorporates heating of the carbonaceous material to incandescence, by its partial combustion to carbon dioxide, with or without added inert materials. For example, the carbonaceous material may be coke or petroleum coke produced by the process, with or without added amounts of natural or synthetic cracking catalysts, or additional inert solids. Alternately, the solid material may be carbon coated inert catalysts and the carbon may be burned off by the combustion to a heated clean catalytic solid. This invention further comprises forming a continuous cascade of the hot, carbonaceous material in sufficient amount to provide adequate sensible heat content for the several purposes of:

1. Complete distillation by a “snowflake on a hot stove” method;
2. Vapor phase cracking of the heavier fractions;
3. Contact coking of residua;
4. Decomposition (thermal reforming) of paraffins to olefines and naphthenes to aromatics;
5. High temperature cracking processes (1500°-2000° F.) such as the production of ethylene, propylene, butadiene, etc.

This invention further contemplates the formation of a cascading curtain of the initially incandescent solid material within the containing vessel and the spraying of whole and reduced crude oils and recycled light and/or heavy oils and vapor and gases onto the cascading curtain of material at one, two, or more horizons.

This invention also incorporates provision for the metered withdrawal of a plurality of vapors at several successive horizons of the annular carbonaceous cascade so that the first vapor will consist of the lightest fractions, the intermediate vapors will be comprised of the heavier fractions with their cracked products and the lower vapors will consist of the products resulting from the final contact coking residua and their vapor phase cracked products. The invention particularly provides for the accurate control of the degree of vapor phase thermal cracking of any fraction by varying the time of contact with the source of heat through controlled venting and withdrawal. Thus, no fraction need be over-cracked, nor must any heavy fraction be withdrawn without sufficient thermal treatment.

This invention also provides for the very rapid removal and stabilization of cracked products in order to minimize polymerization and thermal decomposition. This is accomplished either by rapid quenching and/or by superheating each effluent stream by admixing very hot hydrogen for superheating so that the temperature of each vapor stream is raised well above the initial dew point of its heaviest component and then promptly conducting the vapor stream entrained in the thermal carrier over a catalyst in order to assure that no unwanted reactive olefines are produced in the system and that all gases and all distillates are rendered unreactive and stable by vapor phase catalytic hydrogenation coincidental with the removal as hydrides of any oxygen, nitrogen and sulphur which may be present. It follows, therefore, that not even recycled stock to the incandescent annular cascade will contain polymerizable compounds or alkyl reactive groups.

In the same multivapor petrofiner system and concurrently with the multifunctional processing of the feedstock crude oils, light paraffins and naphthenes (some of which are formed during catalytic desulphurization) can be decomposed (thermally reformed) to olefines and to aromatics. Thus, the gasoline produced can, when desirable, consist chiefly of olefines and aromatics. Furthermore, jet fuels can be routinely produced with any specified aromatics content when incorporating solvent extraction or hydrogenation to naphthenes.

Further, the multivapor petrofiner can be concurrently used for various high temperature decomposition reactions such as the cracking of butane at temperatures in the order of 2000° F. for the optimum yield of ethylene.

This invention further provides that some of the permanent gases generated by the process, such as methane, will be thermally cracked to hydrogen and elemental carbon and simultaneously heated in a separate portion of the same apparatus or a similar separate apparatus. Thus, there need be no outside source of hydrogen nor of fuel. The cracked methane stream can be quenched by water to retain and separate acetylene.

This invention also provides for hydrogen, generated by thermally cracking the necessary amount of permanent gases and heated above 2000° F., to be tempered by cooler hydrogen and admitted to multivapor products to supply a suitable partial pressure of hydrogen and adjust each vapor stream to optimum temperature for catalytic vapor phase desulphurization and for the saturation of polymerizable molecules.

This invention additionally provides for the thermal reforming of selected vapor streams subsequent to desulfurization according to specifications desired by prospective purchasers.

It is also incorporated in this invention that whatever nonvolatile materials such as salt, metallic compounds and residual fixed carbon remain with the solid fuel cascade and that the upgraded liquid distillate product will thereby be desalted, demineralized, and upgraded to contain only readily salable components.

Severe hydrodesulphurization can be performed upon the primary vapor streams produced in this invention without the regard necessary in conventional systems for the coincidental saturation of olefines and aromatics because this invention provides a convenient and economic means of thermally reforming any number of recycled or separately introduced side streams by introducing them into a cascade of very hot solid carbonaceous materials. Moreover, the vapor streams may be deliberately saturated by catalytic hydrogenation so that thermal reforming may be uniformly performed to yield a minimum of permanent gases and a maximum of desirable liquid hydrocarbons.

All of the heat for the system is provided by the partial combustion of anthracite coal, coke, petroleum coke or other suitable solid hydrocarbonaceous or carbon coated inert materials to carbon dioxide in oxygen. Hydrogen for the system is furnished by thermal decomposition of reformed fractions and, when necessary, is supplemented by the thermal cracking of methane generated in vapor phase cracking and hydrogen stripping operations. Thermal control of vapor streams subjected to catalytic desulphurization is effected by the admixing of hydrogen in suitable temperatures.

The distillation of the liquid oil feedstock in this invention incorporates a "snowflake on a hot stove" concept, so termed because of the similarity of snowflakes dropping on a very hot stove and immediately vaporizing to the oil feedstock droplets contacting the vapor incandescent cascade and immediately vaporizing. Further, the vapors produced in the distillation function may be instantly removed from the heat source, quenched by hydrogen and/or light hydrogen carbon and maintained in a vapor phase by reducing the partial pressure
of the heavier constituents in order that complete vapor phase desulphurization and saturation may be promptly performed on each product stream.

This invention is entitled "The Multivapor Petroformer" because a plurality of hydrocarbon vapors may be continuously withdrawn from the system at measured and controlled rates. The quality of the several vapors can be accurately controlled so that, for example, one or more vapors may be comprised entirely of straight run distillates or one or more vapors may consist chiefly of vapor phase cracked products of any higher boiling range distillate. Moreover, the multivapor system of this invention incorporates in a single continuous operation such usually complex petroleum refinery functions as (1) topping off straight run gasoline, (2) distilling and removing as a separate vapor any desired boiling range fraction, (3) coking of residua, (4) vapor phase cracking of any higher boiling range fraction into products of predictable molecular weight, (5) decomposing selected recycled streams of C₆, C₇, C₈, etc., paraffins to olefins and deposing naphthenes to aromatics, and (6) high temperature (in the order of 2000°F.) cracking reactions, such as the production of ethylene, propylene, butadiene, etc. from butane, propane and ethane.

As is explained here below, selected vaporized distillate fractions may be subject to high temperature thermal and/or catalytic treatment during accurately controlled periods of time as short as a few hundredths of one second when required. Furthermore, two or more such vapor streams can be introduced into the same vessel and subjected to separate and accurately controlled thermal treatment.

It should be pointed out here that no other device in the petroleum industry removes more than a single composite vapor from any catalytic or thermal cracking operation while this invention can remove from the same vessel simultaneously many separate vapor streams which have been subjected to separate thermal treatment. Therefore, rather than over-treating the more easily cracked components while under treating the more resistant fractions, as is the case in all other cracking and coking systems, this multivapor method can accurately control the time-temperature history of each separate effluent stream.

This invention replaces the multitude of pipestills and heated coils, heat exchangers, reformers, crude oil toppers, coking drums, cracking stills, catalytic crackers, etc., which are standard equipment in the modern refinery.

Other objects of the invention will be pointed out in the following description and claims and illustrated in the accompanying drawings which disclose by way of example the principle of the invention and the best mode which has been contemplated of applying that principle.

In the drawings:

FIGURE 1 is a schematic illustration of an integrated vertical retort vessel showing the annular cascade of solids, the mechanics of their partial combustion to carbon dioxide, and the manner of transferring heat from the hot solids to the oils, vapors, gases under treatment, and also includes a flow diagram of the various fluid streams of the system.

FIGURE 2a is a schematic illustration of the high temperature butane cracking and ethylene production section and the thermal reforming sections which lie below the system feeder shelf.

FIGURE 2b is a schematic drawing of that section of the vertical retort vessel directly below that shown in FIGURE 2a and performed the functions of topping the oil under treatment, distilling and selectively cracking heavier fractions, coking the residua and removing a plurality of separate vapors therefrom.

Basically, when operated as an upgrader of off-grade whole and reduced crude oil feedstock, this invention includes an essentially once-through process whereby the crude oil is desalted and demineralized by distillation, the residual content is eliminated by contact coking, and wherein all products are removed as nitrogen, sulfur, and oxygen; and reactive olefins are saturated and rendered stable by catalytic hydrogenation.

The vertical retort shown in FIGURE 1 receives solids, liquids and vapors and discharges solids and vapors. FIGURE 1 includes the flow sheet diagram of both an annular cascade of solid carbonaceous materials and the fluid flow of the process. The term "solid carbonaceous materials" and the like used herein also includes any accompanying inert or catalytic materials, or carbon coated refractory catalytic materials.

The apparatus of the subject invention is, except for the sections shown in detail in FIGURES 2a and 2b, a unique combination of constructions shown and described in detail in my prior copending applications Serial No. 17,293, now Patent 3,083,471; Serial No. 41,679, now Patent 3,107,985; and Serial No. 186,920. More specifically, the apparatus includes a relatively large vertical pressure vessel 50 having a number of bins such as bins 1, 3, 16, 23, and 35, which may be closed by suitable bell valves 2, 4, 20, 21, 22, etc., as shown schematically in FIGURE 1. Two adjacent bins, such as 1, 3 and their associated bell valves may constitute a pressure lock. Suitable valved inlets and outlets, such as valved inlet 5 and valved outlet 6 in bins 3 are provided for each of the pressure locks as may be necessary.

Within the pressure vessel 50 there are a number of gyatory shelves, which may be solid material feeders and/or gas isolating separators. See gyatory shelves 8, 13, 14, 30, and 32. Each of these gyatory feeder shelves may carry solid materials in a sufficient density and depth thereon to effectively prevent gas diffusion from one side thereof to the other to thereby create gas isolated sections within the pressure vessel 50. The gyatory shelf mechanism also feeds the solid materials by providing a controlled annular cascade of solid materials over the periphery thereof, and the structure and operation of such shelves is described in detail in my copending application Serial No. 17,293, filed March 24, 1960, now Patent 3,083,471. Reference may be had to this copending application for the mechanical details of the gyatory shelf mechanisms, and the like.

Also within pressure vessel 50 there are two partial combustion chambers 12 and 31 for the heating of solid carbonaceous material, such as coke, by its partial combustion to carbon dioxide. Dual oxygen injection and a CO₂ offtake are provided for each partial combustion chamber. Rather than burden the disclosure with a detailed explanation of the operation of these partial combustion chambers, reference may be had to my copending application Serial No. 186,920, filed April 5, 1962, for a detailed disclosure of the construction and the method of operation of partial combustion chambers 12 and 31.

Also contained within the pressure vessel 50 is a methane cracking and hydrogen heating zone 33 which is similar to a zone of this type described in detail in my copending application Serial No. 41,679, filed July 8, 1960, now Patent 3,107,985, and reference may be had to this copending application for the construction and operation of methane cracking and hydrogen heating in great detail.

In addition to the pressure vessel 50 and the adjuncts of pressure admitting and discharging valved lines for the pressure locks described above, there are various metered oxygen intakes for the partial combustion zones and said copending application, as well as CO₂ offtakes for the partial combustion zones together with mechanical cleanouts and knockout drums. There further is provided means for introducing varied fluids into the system as will be described in connection with the method.

The principal novel apparatus features of this inven-
tion resides in a hydrocarbon stripping and reforming section 9, illustrated in detail in FIGURE 2a; and a distillation, cracking and contact coking section 15, shown in detail in FIGURE 2b. The distillation, cracking and contact coking section 15 has a conduit 18 with a metered valve 91 therein for controlling the admission of crude oil and recycled oil into the system from a spray head 17 onto a deflecting cone baffle 40. The distillation cracking and contact coking section 15 is directly below the hydrocarbon stripping and reforming section 19, although by suitable controls there is only minimal intermixture of the gases therein.

Within the distillation section 15 there are a number of vertically spaced vapor offtakes. The first vapor offtake 44 is above the crude oil inlet spray head 17 and includes a deep radiant shielding skirt 86 for shielding the spray head from the radiant heat of the annular cascade of hot solids. Below the spray head 17 are a plurality of additional vapor offtakes. While any number of such offtakes may be employed, there are illustrated at 41, 42, and 48. Vapor offtake 48 may have a shortened offtake cone, while vapor offtakes 41 and 42 may have deep skirts 87 and 88 to confine and constrict the annular cascade of hot solids. The core baffle 43 is to prevent boiling up of the solid materials and it spreads the hot hydrogen stream 44 upward into contact with the falling cascade of hot solids for the purpose of purging vapors from the spent fixed carbon of the solids. Below the last vapor offtake, there is a core baffle 43 which in turn is positioned above a purge hydrogen inlet 74.

Each of the vapor offtakes is connected to a knockout drum and dust precipitator schematically illustrated as drums 57, 61, 66 and 67, and mechanically cleared offtake duct leads from each offtake cone to the associated knockout drum. Behind each knockout drum there is a controllable positive displacement valved metering device such as valued metering devices 46, 62, 67, and 71.

In the hydrogen stripping and reforming section of FIGURE 2a there are a plurality of spray cone inlets, 103, 108, and 110 connected to metered inlet lines. Immediately below the inlets are skirted cone metered outlets 105, 109 and 111. Separated quench inlets 97, 96 and 95 are also provided as shown.

Referring again to FIGURE 1, the flow diagram schematically shows additional elements which are well known in the petroleum refining art. These elements include desulfurizing and saturating catalyst chambers 47 and 64, a primary fractionator 60, primary condenser 59, a secondary fractionator 114, a secondary condenser 117, and various lines, pumps, coolers, etc. as normally employed with such apparatus, but connected as shown in FIGURE 1.

The operation of this process may be described as follows: Solid carbonaceous material, preferably coke resulting from the process, is crushed so that the terminal velocity of the freely falling particles in the gases encountered will, for example, be between 5 and 30 feet per second. Occasionally mixed with the ground carbonaceous material may be larger pellets of hard coke and/or fragments of refractory material added for the purpose of breaking and scouring scabs and accretions from the internal walls of the retort. For certain purposes, catalytic material may also be added to the crushed carbonaceous material.

The charge material is elevated by skips or by some other suitable means and is dumped into measuring bin 1. Through the operation of bell valve 2, the solid charge material is admitted into the charging lock 3. Charging lock 3 is cyclically pressurized and depressurized with carbon dioxide from flue gas receiver 7, regulated by inlet valve 5 and vent valve 6. By further cyclic operation of the charging lock, and by closing bell valve 2, pressurizing lock 3 and subsequently opening bell valve 4, the contents are dumped upon a gyratory system feeder shelf 8.

Gyratory feeder shelf 8 provides a uniform annular cascade of solid fuel which, when dropping freely into a solids preheat chamber 10, will flow concurrently with hot carbon dioxide admitted through duct 11, which originates as a product of combustion from the partial combustion distillation 12.

Carbon dioxide used for preheating of the carbonaceous charge is withdrawn at duct cone 52 from chamber 12. The carbon dioxide from cone 52 is conducted through knockout drum 53 and cooler 26 to flue gas receiver 7. This gas may be used to pressurize charging lock 3. The carbon dioxide from chamber 12 is cooled and treated in a knockout drum 9 and may then be recycled to the coke preheating zone 10 through duct 11.

At the lower end of the preheating zone 10, the preheated charge material forms a deep separating bed whose depth is controlled by the variable amplitude and gyrating rate of shelf 13 reacting a gamma ray density sensing apparatus or other suitable level control device. By controlling the system so that there is practically no pressure differential across bed 13, the deep bed of preheated solids effectively prevents the very hot carbon dioxide in partial combustion zone 12 from flowing counter-currently around its edges and the freely falling carbonaceous material which occurrence would result in the undesirable formation of carbon monoxide. Causing the very hot carbon dioxide to flow concurrently with the carbonaceous material in preheating zone 10 insures against the overheating of the carbonaceous material and practically eliminates the formation of carbon monoxide from the carbon dioxide and carbon.

The process heating of coke or other carbonaceous material by its partial combustion to carbon dioxide in chamber 12 by the dual admission of oxygen is, as mentioned before, described in detail in my copending application Serial No. 186,920, filed April 12, 1962.

The charge solids heated by its partial combustion to a temperature in the order of 1500° F. to 2500° F., or even better, according to the requirement of the process, accumulates upon separating shelf 14 to form another deep separating bed suitably controlled in depth by a density sensing device, and this bed serves to separate the zone of oxide gases from the zone of hydrocarbon vapors. Because the oxygen is metered into zone 12 and the carbon dioxide metered out and because crude oil and vapors are likewise metered in and out of the zones 19 and 15 on the other side of shelf 14 the deep separating bed on gyrating shelf 14 efficiently eliminates the diffusion of oxide gases into the hydrocarbon stripping and reforming zone 19. That is, the various metering devices on the inlets and outlets of each zone insure against any substantially pressure differential existing across separating shelf 14.

The gyratory shelf 14 operates in the manner described in my aforesaid copending application Serial No. 17,293, now Patent 3,083,471, and provides a uniform annular cascade of solid incandescent material which falls freely through hydrocarbon stripping and reforming zone 19. For example, ground freely falling coke may enter the hydrocarbon stripping and reforming zone 19 at a temperature as high as 2500° F. (unless it is intentionally cooled by adding solid material at a lower temperature or by reducing the rate of combustion oxygen flow in the partial combustion zone 12). The coke continues to fall through the distillation cracking chamber 15 and finally reaches surge bin 90 at a temperature in the order of 1300° F. after having supplied the sensible heat for stripping and reforming of hydrocarbon gases and for the distillation, vapor phase cracking and contact coking of the crude oil and recycled heavy bottoms which liquids are admitted into contact with the coke through spray head 17 duct 18, measured by meter 91. The annular cascade of very hot solid materials there-
fore provides the heat to accomplish the stripping, reforming, distillation, vapor phase cracking, and contact cooking of the various feed products which may include vapors, gases and liquids. The liquids will immediately be vaporized upon contacting the hot annular cascade and then may be treated and withdrawn as vapors. The hydrocarbon stripping and reforming zone 19 and the lower contiguous distillation, cracking and contact cooking zone 15, will further be described in detail below.

The crushed coke cascade may be increased in amount and capacity over that of entering the system through charging lock 3 by recirculating coke between surge bin 90 and separating feeder shelf 13 as is explained in my copending application Serial No. 266,255, filed March 19, 1963. Surplus application for recycling in zone 31 the solid carbonaceous materials is not shown herein for the sake of simplicity.

The material in surge bin 90 is retained by turnip valve 20 in order to allow the gas tight closing of turnip valves 21 and 22 and pressure change coke transfer lock 23. Coke transfer lock is pressurized by carbon dioxide raised to a suitable pressure by compressor 24 pressurizing receiver 25. The source of carbon dioxide may be from the combustion product from partial combustion zone 12 which is cooled and stored in flue gas receiver 7.

Evaporation and combustion of turnip valves 20, 21 and 22 and coke transfer lock pressurizing valves 28 and 29, coke is admitted to surge bin 27 at a somewhat higher pressure than exists in the upper part of the system comprised of zones 10, 12, 15 and 19. Gyroratory shelf 30 now becomes the system feeder for the methane cracking system and the hot solid material, which now contains whatever salts and fixed carbon which may have been extracted from the treated crude petroleum, falls as a annular cascade into the secondary partial combustion zone 31 where the solids are raised above 2500 F. by partial combustion of carbon to carbon dioxide. The method of partial combustion in zone 31 may also be carried out in a manner similar to that in zone 12, and as fully described in my copending application Serial No. 186,920.

The re-heated high temperature coke falls upon gyroratory shelf 32, the accumulation of which forms a deep separating bed between the secondary partial combustion zone 31 and the methane cracking and hydrogen heating zone 33. Gyroratory shelf 32 again feeds the incandescent coke in an evenly distributed annular cascade in order to optimize heat transfer between gases and solids in zone 33. The re-heated cascade of gasified solid material, falling freely through zone 33, furnishes the sensible heat for heating of methane and to accomplish its thermal decomposition to hydrogen and carbon dioxide. Methane recycled from the system is introduced through metered inlet 54, contacts the falling coke at 2500 F. or above, and is cracked into hydrogen and carbon. Both hydrogen and carbon black which leave the system above 2000 F. through offtake 55 above core baffle 56 and the hot hydrogen may be used to furnish heat for the superheating of vapor streams before catalysis in order that no liquid mist remains to coat the catalyst.

The cracked product steam in line 73 may be utilized for the production of acetylene by admitting the stream through valve 122 to a quencher 123, followed by a compressor 124 and adsorber 125; thereby extracting nearly pure acetylene by water absorption as is well known in the art.

Having furnished the sensible heat for methane cracking and the heating of the cracked products, the anular solid material cascade may still contain substantial heat which may be recovered by various means. For example, methane and recycled hydrogen from the scrubber and absorber may be introduced into the cascade above bin 34 (not shown) and the coke will then reach the discharge surge bin 34 at a temperature in the order of 300 or 400 F. The spent solids containing whatever salt, fixed carbon and other solids removed from a heavy oil undergoing treatment, is then discharged from the system by the suitable operation of discharge lock 35 being alternately pressurized and depressurized with carbon dioxide which is a flue gas from the primary combustion chamber.

Since the solids are continuously increasing in amount, some of them may be recycled and part rejected (by conventional apparatus, not shown), thereby allowing for the continuous removal of salt and other nonvolatile and noncombustible solids.

The flow path of the cascading solids has been described together with the flow path of the heating gases and vapors. The flow path of the distilled and thermally cracked vapors will now be described in connection with FIGURES 1 and 2 (2a and 2b).

Referring first to FIGURE 25, crude oil and recycle oil at about 200 F. is admitted through duct 18, metered by meter 91 and sprayed against the hot annular cascade of incandescent solids through spray head 17 after being deflected off cone 40. It is also contemplated that solid organic matter such as pitch precipitated from petroleum and/or pulverized coal can be entrained in the recycle and crude oil stream and sprayed against the hot annular cascade to effect carbonization and partial conversion to useful liquids.

The vapors indicated by arrows 39 are those which have the lowest boiling range of about 300 F. and therefore, distill first and constitute the familiar refining function of "topping." The vapors from the initial distillation immediately leave the source of heat in the zone 15 and are subject to no further thermal treatment, but is desulfurized after being brought to temperature by the admixing of hot hydrogen. The vapors pass from the first vapor offtake 44 through mechanically cleaned offtake duct 45, knock-out drum and tar precipitator 57 and are metered through positive displacement meter 46 and thence to line 58. For desulfurization of this vapor it is passed through conduit 63 to desulfurizing catalyst chamber 64 and catalytically hydrogenated in a manner similar to the other vapor streams as will be described. It will be noted that the vapors first produced are those of low molecular weight and hence require no thermal cracking to yield molecules in the gasoline weight range and possibly therefore be immediately removed from the system, desulfurization not necessarily being necessary.

The crude oil feedstock is progressively and very rapidly heated as it falls through the distillation and cracking zone 15 in contact with the annular solids cascade. The liquid absorbs heat very rapidly and distills off vapor of progressively heavier and heavier molecular weight. Such heavier vapors can be withdrawn directly into subsequent vapor offtake cones 48, 41 and 42 or, through proper metering, can be forced to pass concurrently with the very hot annular cascade of ground solids and thereby be subjected to any desired degree of thermal cracking. For example, whatever vapor is boiled off below spray baffle cone 40 and offtake cone 48 can, by suitable metering of the various vapor outlets, be forced to flow concurrently with the descending fuel cascade and be drawn off through offtake cone 41, or, if more extensive thermal treatment is required, the vapors can be forced to remain even longer with the hot solid material cascade and be metered from the cracking zone, e.g. through cone 42.

As a further example, all of the heavier molecular weight vapors beyond the very lightest can be made to suffer thermal alteration by merely closing all outlet valves on the second, third, and fourth vapor offtakes, offtakes 48, 41 and 42 thus forcing all of the vapors to pass counterconcurrently up against the descending hot solids cascade to be withdrawn through cone 44. In this manner, for example, the lighter and lower boiling hydrocarbon would be subject to no thermal treatment other than simple distillation, while the heaviest and highest boiling fractions could be subjected to the most severe thermal cracking.
Likewise, the medium boiling range components would receive only moderate thermal treatment. Through incorporating a suitable number of such vapor offtakes and by varying the rate of metering, a wide variety of cracked products can be made by this very efficient system. At the same time, the crude oil has completely changed its form and the product is solely that of a distillation with varying amounts of cracked molecules with an upper boiling range to suit any refiner's customer's specifications. It is, therefore, evident that the particular number of offtakes shown is by way of non-limiting example only.

A mechanically cleared offtake duct from cone 48 directly passes through a knockout drum and tar precipitator 61 and then through a controlled or valve metering device 62 into line 63. Next, the vapor and hot hydrogen, which is admitted through line 76, is passed into a first desulfurizing and saturating catalyst chamber 64 (chamber No. 1), for catalytic hydrogenation of the vapor to remove and prevent the formation of chemically troublesome compounds. Thus, organic compounds which contain functional groups of oxygen, nitrogen, and sulphur are completely destroyed. Also, this treatment avoids the polymerization of reactive unsaturated hydrocarbons into undesirable large molecules which form asphalts and tars. The output from the catalyst chamber 64 is line 65 which leads into primary fractionator 60.

The vapor from the third offtake, offtake cone 41 also goes through a mechanically cleared offtake flue into a knockout drum and tar precipitator 66 and then through a controlled valve metering device 67 to a line 68. The vapor is then directed to another desulfurizing and saturating catalyst chamber 47 (No. 2) after being combined with a stream of hot hydrogen admitted through line 75. The function of this desulfurizing and reforming catalyst chamber is the same as catalyst chamber No. 1, but different catalyst chemists may be tailored to different results, e.g., to produce different specific products. The offtake then passes through line 69 to primary fractionator 60.

From the fourth vapor offtake 42, the thermally cracked vapor can pass through mechanically cleared offtake duct, a knockout and tar precipitator 78, and a controlled metering valve 71 into line 72. After being mixed with hot hydrogen admitted through line 76, the vapors then pass into No. 2 desulfurizing and saturating catalyst chamber 47.

When demineralizing feedstock oils which contain volatile metallic compounds which may distill over at cracking coke temperatures, a separator may be included in line 72 (not shown) to confine such metallic volatiles into separate streams for redistillation at lower temperatures.

Hot hydrogen and some carbon black removed from the methane cracking and hydrogen heating zone 33, through offtake cone 55, pass through line 73 and are introduced into zone 15 through hydrogen inlet 74. Additional hot hydrogen mentioned above passes through line 75 to be mixed with the vapors passing to the desulfurizing and reforming catalyst chamber 47. Hydrogen also passes through line 76 to be mixed with the vapors going into desulfurizing and reforming catalyst chamber 64. The hot hydrogen is thus introduced into each vapor stream so that when necessary, the temperature of the steam is raised well above the initial dew point of its heaviest component. The stream is then conducted as a thermal carrier hydrogen over the catalyst in the chambers to insure that no reactive olefines remain in the system and to further insure that when required and desirable, all gases and all distillates are rendered unreactive and stable by vapor phase catalytic hydrogenation.

From the primary fractionator 60 the heavy bottoms are moved by pump 77 through line 37 for recycling. The bottoms pass through a surge tank 78. Valve 79 controls the admission of the recycle bottoms into the inlet cone 38, which in turn is controlled by meter 91. The crude oil to be treated may be admitted from a ship or pipe lines through system inlet 36 and is controlled by suitable valve 86 for admission into line 38 to be injected into the system, and as mentioned above the whole or reduced crude oil feedstock may incorporate other materials.

Cold reflux is admitted through intake 30 to the primary fractionator 60, while solids-free heavy product distillate (jet fuel, diesel fuel, stoke oil) passes out of the fractionator through offtake 81 and is cooled in heat exchanger 82 before removal through a product distillate line 83.

The overhead from the primary fractionator 60 goes to primary condenser 59, and from condenser 59 the condensed product passes through offtake 85 to be directed to a thermal reformer (not shown). The overhead from condenser 59 includes saturated gases which pass to a primary scrubber and absorber (not shown) through line 84. Then some of the gas from the scrubber and absorber, including the methane and other permanent gases, may be recycled through intake cone 54 for cracking of the methane so that all of the hydrogen used is generated in the system itself and no outside source of hydrogen is necessary.

Butane, propane, propylene, etc., can be separated from the intermediate and final product streams for the manufacture of alkyl and polymer gasoline, which is standard practice. Surplus butane, propene, pentane, etc. can be returned to the multivapor column and subjected to precise heating and quenching in order to produce butylene and propylene for greater yield of alkyl and polymer gasoline.

The zones 15 and 19 may be operated at varying pressures ranging from less than 1 to 30 or more atmospheres provided that the partial pressure of hydrogen is sufficient to allow the vaporization of desirable fractions.

For the purposes of rapid quenching of certain selected vapors in the various vapor takeoffs in the distillation, cracking and contact cracking cone 15, there is provided a quenching stream in line 92 with side branch inlets 93 and 94 for supplying quenching gas to vapor offtakes 41 and 42. Distributing baffles plates 98 and 99 are provided for the quenching gas inlets 93 and 94 respectively so that the quenching gas intimately mixes with the vapors being taken off to rapidly quench the same. The quenching gas may be hydrogen or it may be recycled light hydrocarbon vapors.

As shown in detail in FIGURE 2a a hydrogen stripping and reforming zone 19 includes a teapot section providing an incomparably efficient and economical means for manufacturing ethylene, propylene, butadiene, etc., from refinery gases, while the next two lower sections provide means for reforming of certain liquid streams as they are recycled. Referring specifically to the apparatus, below the feeders shelf 14 and within the annular cascade there is an inlet cone 103 connected to a metered inlet line 104 for introducing ethane, butane, propane, etc., into the hot annular cascade. Below inlet cone 103 is an offtake cone 105 with a relatively deep skirt 107. The depth of the skirt 107 on the outlet cone is predetermined in accordance with the other variables of the process. The incoming gases are admitted with the hot annular cascade and may be withdrawn through the offtake cone 105 and metered offtake line 106 while at the same time being quenched with the quenching gas (hydrogen or recycled ethylene) through an inlet 97 below a quench gas baffle 102. The very hot annular cascade reforms or cracks the incoming products into ethylene, propylene, butadiene, etc., depending on the particular incoming feed gas.

Within the same pressure vessel 50 and below the ethylene production section there is a reforming section which may be composed of any number of liquid inlets and vapor offtakes. For example, through a metered valve
inlet cone 108. C₆ plus reforming stock from primary condenser 59 may be introduced into the annular cascade and they may flow downwardly below the skirt of offtake cone 109 while being reformed and then pass out through a metered valve offtake. A quenching stream 96 below a quenching baffle 101 may also be provided. In the next section immediately therebelow, a heavier reforming stock in the range of 200°F to 400°F, may be introduced through a metered valve inlet cone 110 and pass around the skirt of offtake cone 111 to pass through a valve metered offtake duct into a reformed stream line 112. Again, a quenching gas may be introduced through inlet 95 below a quenching gas spreader baffle plate 100. Thus, two or more reforming stock streams may be subjected to different thermal treatment, in the way of hydrogen stripping operation.

Of course it will be understood that the skirts of the various offtake cones may be of different lengths depending on the time of thermal treatment desired. Also, it is to be noted that the schematic that the various supports, insulation, etc., which of course are necessary in the very high temperature environment, have not been shown for the sake of simplicity.

The reformed vapor stream in line 112 passes to secondary fractionator 114. Cold reflux may be admitted through inlet 120 into secondary fractionator 114 and the bottoms from fractionator 114 pass out through line 115 to be introduced into the lower portion of primary fractionator 60. Heavy Product Gasoline may pass off the secondary fractionator through line 121 and the overhead from the secondary fractionator goes to a secondary condenser 117. Light product gasoline passes out as a liquid from the secondary condenser 117. From the gas outlet of condenser 117, secondary unsaturated gases pass to an absorber (not shown).

As can be appreciated from the foregoing, there are a relatively large number of variables which can be controlled to control the various functions of the system. In the cascade of solid materials; the temperature of the cascade may be controlled, the proportionate amount of carbon inerts in the cascade may be controlled, the particle size and average terminal velocity of the materials in the cascade may be controlled, and the particle ratio of surface area to volume may be controlled. In liquid phase cracking, the partial pressure of the heavier components and the system pressure, can be controlled to determine the time required to vaporize and therefore the time at which the heavier components are in contact with the hot cascade. Furthermore, control of vapor phase cracking is also offsite control for use for the offgas. The vapor and the time the vapor is allowed to stay in the hot incandescent cascade, the rate of vapor draw-off and the rate and degree of quench either by hydrogen or other permanent gases. Also, the admission of hydrogen, either hot or cold, to the product streams in a molecular ratio of 2:1 to the hydrocarbon vapor, may be used to control the heat capacity and to provide a wide range of adjustments in the process.

The use of the term “solid carbonaceous materials” and similar terms as used in the claims for the solid material, intended to include all suitable solid materials and inerts carried thereby. For example, the feedstock could consist of ground coke and other suitable material such as petroleum coke or anhydrite coal and various inerts may be incorporated therein which would also be heated up and carried through the system. Further heated refractory catalysts or inerts, or carbon containing materials can be used for the cascade.

The liquid petroleum feedstock could be whole or reduced crude oil which could be used plain or with suitable admixture not only of recycled bottoms but also of solid hydrocarbonaceous organic matter such as asphaltene and pulverized coal entrained in the recycled stream to effect carbonization and conversion to useful liquid molecules.

As can be seen from the foregoing, the usual separate refinery operations are combined in a single system. Furthermore, by controlling the metering of the various vapor offtakes, various products may be produced to customer specification. The only input materials to the system need be the solid feedstock, a liquid feedstock, a vapor feedstock, or combination of the three. The inert and heating CO₂ gases used in the system are produced within the system and the hydrogen used in catalytic hydrogenation is also produced within the system. The residual or heavy bottoms are recycled and further treated in the contact cracking zone and the resulting products may be either straight-run distillates or vapor phase cracked products.

It is further noted that the different vapor streams may be subjected to separate and accurately controlled different thermal treatment by means of the process disclosed. In addition, high temperature decomposition reactions as well as reforming may take place concurrently in the vessel. The products of feedstock oil distillation are saturated so that subsequent thermal treatment will result in a high proportion of valuable products.

1. A method of upgrading crude oil comprising: contacting crude oil with a free falling cascade of solid carbonaceous materials at a temperature sufficient to distill crude oil and in sufficient amount to provide adequate sensible heat for distillation of the crude oil and thermal cracking thereof, introducing said crude oil into contact with the free falling cascade of solid carbonaceous materials during the free fall thereof, providing a hydrogenation environment for said contacting, selectively withdrawing hydrocarbon vapors from a plurality of different horizons adjacent the point of contacting the crude oil with the cascade so that different and mixed vapors may be withdrawn from different horizons, and catalytically treating at least some of the so withdrawn hydrogen entrained vapors to saturate with respect to hydrogen and to remove organically combined oxygen, nitrogen and sulphur as respective hydrates.

2. A method as defined in claim 1 further comprising, initially heating the solid carbonaceous material to the required temperature by its partial combustion in a closed gas isolated chamber.

3. A method as defined in claim 1 wherein the contacting of the crude oil with the cascade of solid fuels is accomplished in a closed chamber, and the catalytic treatment of the cracked crude oil vapors is accomplished under controlled temperature conditions.

4. A method as defined in claim 3 further comprising, separating methane from the withdrawn and treated hydrocarbon vapors, obtaining the hydrogen for the methane environment by cracking the methane over hot solid carbonaceous materials in a zone separate from the contacting of the crude oil with the solid carbonaceous materials, and recycling selected fractions obtained by fractionating the withdrawn and treated hydrocarbon vapors for contacting the cascade while the cascade is falling to accomplish thermal decomposition of the fractions.

5. Petroleum refining method comprising, spraying feedstock crude oil into an incandescent cascade of solid materials at an incandescent temperature sufficient to cause distillation and cracking of said feedstock crude oil and in an amount having sensible heat available for the distillation and cracking while the solid material is falling within a closed chamber and in a hydrogen environment, distilling the lighter fraction of said feedstock crude oil by the contacting thereof with the incandescent cascade of solid materials and selectively and controllably thermally cracking the heavier fractions, controllably withdrawing the various fractions from different horizons within the closed chamber, catalytically hydrocracking at least some of the thermally cracked fractions, and further utilizing selected horizons of the cascade for high-
perature cracking of gases and thermal decomposition and reforming of selected streams obtained from the withdrawn streams after fractionation and recycled to contact the cascade.

6. A multivapor method of desalting, desulfurizing and upgrading feedstock oils comprising, heating solid carbonaceous materials to incandescence by partial combustion to carbon dioxide in a closed vertical vessel, providing a free falling cascade of the so heated incandescent solid carbonaceous material in the vessel in sufficient amount to provide adequate sensible heat for all subsequent thermal treatments of feedstock oils, liquids and gases, providing a hydrogen environment in the closed vessel around the cascade contacting the cascade with selected gases at one horizon for thermal cracking thereof, contacting the cascade at another horizon with recycled reforming streams to accomplish the thermal reforming thereof, admitting feedstock oil into the incandescent cascade falling within the vessel, distilling lighter fractions of the feedstock oil and thermally cracking heavier fractions of the feedstock oil as the oil is in contact with the hot incandescent materials, selectively and controllably withdrawing the products of the distillation and thermal cracking as fluid streams from various horizons within the closed chamber, and catalytically treating at least some of the thermally cracked fractions of the feedstock oil stream in an atmosphere of hydrogen.

7. A method as defined in claim 6 further comprising immediately quenching selected ones of the withdrawn streams and superheating each vapor stream of the thermally cracked fractions with predominately hydrogen gas at a temperature above the dew point of the heaviest component of each said vapor phase stream.

8. A method as defined in claim 7 wherein the catalytic treating is accomplished by conducting the vapor stream and hot hydrogen over a catalyst for vapor phase catalytic hydrogenation and coincidental removal of oxygen, nitrogen, and sulphur.

9. A method as defined in claim 8 wherein the feedstock oil contains recycled bottoms and granular solid hydrocarbonaceous materials.

10. A method as defined in claim 8 wherein the hot hydrogen is obtained by thermally cracking methane over hot solid carbonaceous materials in the same system, and further comprising obtaining the methane for the thermal cracking to produce hydrogen from the products of distillation and the gas produced thereby without necessitating using an outside source of methane.

11. A method as defined in claim 10 further comprising rapidly quenching at least some of the cracked methane stream, followed by preforming compressing and absorbing operations on the quenched stream to obtain acetylene.

12. A multivapor method for oil refining comprising, heating to incandescence by partial combustion to carbon dioxide solid crushed carbonaceous materials in a pressurized vertical vessel, feeding the so heated incandescent solid carbonaceous materials in the vessel to provide a free falling cascade in a gas isolated chamber, the solid materials having sufficient in amount to provide adequate sensible heat for subsequent thermal treatment of feedstock oil and recycled reforming streams, introducing crude oil into the chamber and contacting the crude oil with the cascade of incandescent carbonaceous materials to distill off a light fraction and thermally cracked heavier fractions, selectively withdrawing the fractions separately at different horizons from the closed chamber, catalytically hydrogenating at least one of the so withdrawn fractions, fractionating the catalytically treated streams to provide reforming streams, and recycling the reforming streams to contact the cascade for thermal decomposition thereof.

13. A method of upgrading feedstock oil and distilling foreign hydrocarbon containing material carried thereby, such as coal particles and foreign residua, the method comprising; providing a feedstock for the process including crude oil and foreign hydrocarbon containing material, contacting the feedstock with a cascade of solid carbonaceous materials at a temperature sufficient to distill the feedstock, the amount of carbonaceous materials being sufficient to provide sensible heat for such distill and for thermal cracking, providing an environment of hydrogen for such contacting, selectively withdrawing hydrogen entrained hydrocarbon vapors from a plurality of different horizons adjacent the place where the feedstock contacts the falling cascade, and catalytically treating at least some of the so withdrawn hydrogen entrained vapors.

14. A multivapor petrofiner comprising; a pressurized vertical vessel including a plurality of side inlets and outlets for fluid streams, means for feeding a charge of at least initially carbonaceous solid materials under pressure to the pressurized vertical vessel, means for preheating the charge of solid materials in an upper portion of the vertical vessel by combustion gases, means for accomplishing controlled partial combustion of the initially carbonaceous materials to carbon dioxide in oxygen in the vertical vessel below the upper preheating portion, means for feeding the hot partially combusted solid carbonaceous materials vertically downward as an annular cascade into an elongated gas isolated thermal treatment section of the vessel below the partial combustion portion, a plurality of metered inlets into the gas isolated thermal treatment section for introducing fluid streams thereinto at a plurality of horizons, means for causing the introduced streams to intimately contact the falling hot annular cascade of solid materials, a plurality of metered outflows for withdrawing vapor stream products of the thermal treatment in the thermal treatment section, means for introducing a quenching gas into selected outflows, a pressure change lock below the thermal treatment section in the vertical vessel, another section of the vertical vessel below the pressure change lock for accomplishing further partial combustion of the solid materials, and a gas isolated section of the vessel below the last partial combustion section including means for contacting an annular cascade of the hot solids with a gas for cracking the same and removing the cracked product.

15. A multivapor petrofiner method comprising; feeding a charge of at least initially carbonaceous solid materials into a pressurized vertical vessel, accomplishing partial combustion on the solid materials to heat the same, feeding the hot solid materials vertically downward in the vessel after the partial combustion through a thermal treatment gas isolated zone of the vessel, providing a hydrogen environment in the thermal treating zone, intimately contacting for a controlled length of time the falling hot solid materials, first with a gas such as ethane, butane, propane to thermally crack to ethylene, butadiene, propylene, then with at least one recycled reforming stream, then with an oil feedstock including recycled bottoms and entrained fine hydrocarbonaceous solids, rapidly removing the thermally treated fluids in metered amounts at separate horizons in the thermal treating zone, rapidly quenching selected ones of the so removed streams, desulfurizing and catalytically reforming the removed streams of thermally treated feedstock oil in an atmosphere of hydrogen, fractionating the catalytically treated streams to produce reforming fractions, and recycling the reforming fractions of the fractionated stream to the thermal treating zone, reheating the solid carbonaceous materials in a separate isolated zone below the thermal treating zone by further partial combustion, contacting the reheated solid materials with methane produced in the system for thermally cracking the methane, and rapidly quenching at least a portion of the so cracked methane to obtain acetylene.

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