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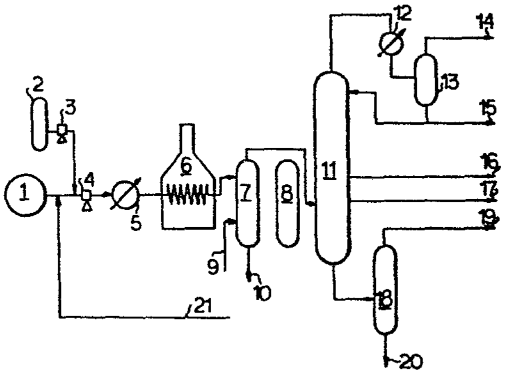
(71) Applicant: **Hayashi Kiyoshige**
1-5-5-205 Higashigaoka
Meguro-ku Tokyo(JP)

(72) Inventor: **Hayashi Kiyoshige**
1-5-5-205 Higashigaoka
Meguro-ku Tokyo(JP)

(74) Representative: **Nöth, Heinz, Dipl.-Phys. et al,**
Patentanwälte Liedl, Nöth, Zeitler Steinsdorfstrasse 21 - 22
D-8000 München 22(DE)

(54) Refining process for producing increased yield of distillation from heavy petroleum feedstocks.

(57) In a refining process for heavy quality oil (16, 17) by means of pyrolysis, the yield of distillation is increased by causing heavy feedstocks (1) to be added with oxide or hydroxide of alkaline earth metal and to be subjected to a thermal reaction i a presence of vapour at the temperature in the range of from 350°C to 550°C under the pressure in the range of from 1 to 20/cm^2.



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REFINING PROCESS FOR PRODUCING INCREASED YIELD OF DISTILLATION FROM HEAVY PETROLEUM FEEDSTOCKS

BACKGROUND OF THE INVENTION

The present invention relates to a petroleum refining process for taking measures to increase products extracted from petroleum feedstocks by means of pyrolysis.

In oil refining for producing intermediate or final products from petroleum feedstocks, heavy feedstocks have hitheto be subjected to one or more processing treatments of a thermal cracking process such as visbreaking, delayed coking and fluid coking and catalytic process such as hydrodesulfurization, hydrocatalytic cracking and fluid catalytic cracking, whereas such treatments, particularly in catalytic process, give rise to many troublesome, knotly problems. The heavy feedstocks include atmospheric or vacuum bottoms, more specifically vacuum distillation residue and further contain topped petroleum residue, atmospheric or vacuum bottoms, heavy hydrocarbon fractions obtained by being subjected to deasphalting or other preliminary treatments, whole crude oils or petroleum derived from coal, shale or tar sands, and tar sand's bitumen. The heavy feedstocks are rich in coke precursors as represented by the typically high Conradson carbon residue content thereof. When such heavy feedstocks are exposed to high temperatures as in a catalytic refining process, a quantity of coke undesirably formed on catalyst surfaces is increased to suffer a lowering of catalytic activity, and therefore, the conventional catalytic refining process entails the disadvantage of false economy because periodic regeneration of catalyst is frequently required. Further, the heavy feedstocks contain a high percentage of heavy metals being principally vanadium and nickel which exist in the form of organometallic complexes. By metals, if in excess, are adversaly affected hydrodesulfurization, fluid ccatalytic cracking, heavy oil cracking, hydrocracking and the other various catalytic reactions. This is because the metals are deposited on the catalysts thereby reducing desirable catalytic activity and selectivity thereof. The metals act as catalysts for dehydrogenation reaction and consequently, hydrogen and coke formations are increased at the expense of desired petroleum products. The heavy feedstocks contain a large quantity of sulfur in petroleum in its condensed state in comparison with distillate such as gasoline, kerosene and gas oil. The sulfur contained in the form of organosulfur complex by the heavy feedstocks is pyrolyzed into H_2S, free sulfur, mercaptan and sulfide, and at the same time, polymerisation and condensation are repeatedly carried out to be gradually turned into extremely complex sulfur compound and further into polyaromatic sulfur complex. In this case, the free sulfur thus formed by the pyrolytic functions as the leading role to repeatedly continue a radical reaction of petroleum analysis and polymerisation/condensation. As a result, coke is increasingly formed due to the polymerisation/condensation and instead, the yield of liquid oil products is diminished and the coke thus formed is heavily redolent of creosote. Coke precursors, heavy metals and suflur are comprehended in great quantities so-called asphaltenes constituting a component of asphaltic fraction in the heavy feedstocks (insoluble component of isopentane). The asphaltenes in the feedstocks are dispersed in heavy quality oils in the form of colloidal solution and show fused aromatic ring constructions with a very large molecules. The asphaltenes have a property of tending to cause further polymerisation/condensation reactions only by being subjected to heat treatment in a distillation process of oil refining and bring about cohesion.

It has heretofore been known to apply a refining process such as fluid catalytic cracking and hydrocatalytic cracking to treatment of heavy feedstocks, whereas these cracking processes entail the foregoing troublesome problem. To solve such a problem there have been proposed various measures. However, any conventional measure comprises turning asphaltene in the feedstocks, which have been soluble on colloidal disperson, into insoluble solid asphaltic fractions in such a manner that they are put on catalyst surfaces at a first stage and heated at the reaction temperature between 400°C and 510°C thereby to segregate and remove the fractions along with the catalysts from the feedstocks, and thereafter, subjecting the fractions thus segregated to hydrogenation reaction, hydrocracking reaction, fluid catalytic reaction and so on by using other catalysts at a second stage. The characteristic clincher for a novel techique of a refining process resides what catalysts are used for adhering thereto and removing solid asphaltic fractions at the first stage. The catalysts adopted at the first stage are generally used in a hydrogen current, and among them those sufferring a lowering of activity to remove the solid asphaltic fractions from the feedstocks are burnt with air and regenerated to recycle.

In passing, it is noted that the inventor has proposed a method (U. S. Patent No. 4,049,538) wherein petroleum feedstocks are, at the first stage in two-stage coking, subjected to heat treatment at the temperature in the range of from 430°C to 520°C with the addition compound of a small quantity (0.5

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- 1.0 weight %) of basic compounds selected from the group consisting alkali hydroxides, alkali carbonates and alkali earth metals with the result that non-crystalline substances thus obtained by the heat treatment are continuously removed, thereby to produce premium needle cokes of high quality at the second stage. Hydroxide and carbonate such as NaOH, Na_2CO_3 and the like in alkali metals bite severely in steel at the high temperature above 400°C. If the heavy feedstocks are pyrolyzed in a molten alkali metal salt in the presence of vapour generated at the temperature in the range of from 760°C to 900°C, coke formation is arrested in producing ethylene, CO, H_2 and CH_4. Furthermore, it has been watched to enable useful gases such as CO, H_2, CH_4 and so on to be produced by supplying powdered coal together with vapour into Na_2CO_3 molten at about 900°C to gasify the powdered coal, whereas there has not yet been established a commercial plant to practicably apply alkali metal compounds to cracking of heavy feedstocks because material having corrosion-resistive against NaOH and Na_2CO_3 cannot be developed.

In brief, oxide and hydroxide in alkaline earth metals do not eat steel even at the high temperature in the range of from 400°C to 1000°C, and besides, even when they are exposed to great quantities of vapour at the foregoing temperature. Oxide and hydroxide in alkaline metals are soluble in water and easy to be ionized, and on the other hand, only a small amount thereof can be dissolved in water even if dissolved and they has a little tendency toward ionization. There is a great difference between the alkaline metals and the alkaline earth metals though they fall under the category of basic compounds.

The inventor has been made a study of a petroleum refining process by using chemicals such as CaO and $Ca(OH)_2$ which do not eat steel even at a high temperature. As a result, the following has been found.

The technique for producing sulfide as the result of the reaction of CaO on sulfur for the purpose of desulfurization is disclosed in Japanese Patent Laid-Open Publication Sho. 46(1971)-629 (Esso Research) which relates to a method for conversion of heavy quality oils, which is accomplished by passing heavy feedstocks through a first bed incorporating fluidized particles containing CaO and passing them through a second bed and a third bed in the same way.

In Japanese Patent Laid-Open Publication Sho. 46(1971)-628 by Esso Research, there is described a method for producing fuel gas, wherein heavy feedstocks are first passed through a fluidizing bed incorporating CaO particles at the temperature in the range of from 800°C to 950°C, and then, they are, at a second stage, passed through a second particle bed at the temperature below 600°C. The both techniques are concerned with desulfurization according to a reaction between Ca and sulfur in the feedstocks and removal of vanadium.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a petroleum refining process for reducing the yield of coke and consequently, increasing the yield of middle oil, particularly distillation oil of good quality in pyrolyzing process for heavy quality oil.

Another object of the present invention is to remove various metals, particularly vanadium and nickel, which are contained in heavy feedstocks and have an effect of accelerating formation of solid asphaltic fractions.

Still another object of the present invention is to suppress appearence of harmful effect of increasing solid asphaltic fractions.

Still another object of the present invention is to increase the yield of refining distillates by condensing vanadium, nickel and sulfur to solid bodies and segregating the solid bodies from coke.

To accomplish the objects described above according to the present invention, there is provided a petroleum refining process for increasing the yield of products extracted from heavy petroleum feedstocks by means of pyrolysis which is carried out by heating in a presence of vapour at the temperature in the range of from 350°C to 550°C a mixture which are obtained by uniformly adding oxides in alkaline earth metals or hydroxides, such as powdered CaO and $Ca(OH)_2$ or slurry dispersed in water to heavy petroleum feedstocks.

BRIEF EXPLANATION OF DRAWING

The single figure is a schematically explanatory diagram of one embodiment of a petroleum refining device according to the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention relates to a petroleum refining process comprising staying, in a presence of vapour, a mixture which is obtained by adding 0.1 to 5 weight % of chemicals such as CaO and $Ca(OH)_2$ to 100 weight % of heavy petroleum feedstocks selected as raw materials while being heated at the final temperature in the range of from 400°C to 550°C thereby to cause a small amount of solid asphaltic fraction to be precipitated along with CaO and $Ca(OH)_2$, permitting heavy metals to act upon CaO and $Ca(OH)_2$ thereby to be precipitated while the soild asphaltic fractions are precipitated, and also permitting H_2S and free sulfur formed at the same temperature in the same reaction time to be precipitated as a result of a reaction on CaO and $Ca(OH)_2$, whereby petroleum intermediates and final products of good quality which contain neither solid asphaltic fraction nor heavy metal can economically be produced with the increased yield due to the coprecipitation of the solid asphaltic fractions, heavy metals and free sulfur.

One of the importances of the present invention consists in a point that the solid asphaltic fractions, so-called "coke", formed by heating the heavy petroleum feedstocks at the temperature in the range of from 400°C to 550°C is sharply reduced at length due to the reaction in a presence of the mixture of CaO and $Ca(OH)_2$ and vapour, and instead, the yield of liquid petroleum fractions, more particularly gas oil fraction is increased. When vacuum residue from Middle Eastern crude petroleum, particularly, Murban/Oman crude petroleum (consisting of 2.3 weight % of sulfur and 13.8 weight % of Conradson carbon residue content) is used as raw material, there were formed 27 weight % of coke, 7.4 weight % of coker gas and 65.6 weight % of coker distillate at the temperature of 530°C in a coking drum. When adding 3 weight % of CaO to the same raw material, there were formed 12 weight % of coke, 8.0 weight % of coker gas and 79.7 weight % of coker distillate at the temperature of 530°C in the coking drum. As evidenced from the experimental results, the yield of the formed coke is remarkably reduced and conversely, the yield of the coker distillate is remarkably increased.

Heavy petroleum feedstocks are different in their components with a kind of the raw materials and contain solid asphaltic fraction which are turned to coke due to heat treatment at the temperature higher than 400°C. The amount of solid asphaltic fractions in vacuum residue is larger than that in atmospheric residue. Therefore, crude oil containing a high percentage of vacuum residue, for example, Daqing crude petroleum and Minus crude petroleum confronts a troublesome problem of the increased coke formation in petroleum refining in comparison with Middle Eastern crude petroleum and inevitably increases the prices of final products. Canadian and Venezuelan tar sand bitumens will bring about far more troublesome problem from the standpoint of refining cost because vanadium and nickel contents thereof are extremely high. The content of solid asphaltic fraction depends upon those of Conradson carbon residue and asphaltene, so that the solid asphaltic fractions are increased with the contents of Conradson carbon residue and asphaltene with the result that the yield of coke formed therefrom is increased. Also, ash and metal components constitute solid asphaltic fractions thereby increasing coke formation thus involved. Vanadium and nickel have an effect to accelerate dehydrogenation of petroleum hydrocarbon and consequently, the yield of carboneus matter is increased. When the least amounts of active carbon, activated alumina, silica gel, activated clay and acidic clay are added as addition compounds into the heavy feedstocks and the feedstocks with the addition compounds are heated, the reactions of hydrocarbon cracking, dehydrogenetion, polymerization and condensation are allowed to progress on the surfaces of the addition compounds thereby turning them into tarry matter and further carboneus matter, the amount of solid asphaltic fractions thus formed is much greater than estimated in view of Conradson carbon residue content and asphaltent content of the feedstocks. Even if heating heavy feedstocks with the least amout of addition compounds such as sulfuric acid, SO_3, SO_2 and free sulfur, a large amount of coke is formed and the yield of solid asphaltic fractions is increased beyond imagination. Accordingly, there has been developed a technique for solution and removal of materials harmful to a real catalyst in FCC and hydrocracking at the second stage in the result of agglutination of the solid asphaltic fraction onto the surface of a catalyst at the first stage, which is used as a preliminary treatment in the FCC and hydrocracking for the heavy feedstocks.

However, it is not negligible that the catalyst (including zeolite, alumina, silica gel, etc.) used at the first stage acts as an accelerator for formation of the solid asphaltic fractions. Furthermore, the formation of the solid asphaltic fractions is also accelerated by various metals such as vanadium and nickel, in the heavy feedstocks. Sulfur compounds are harmful more than metals. This is because as already mentioned above, bridging and polymerisation/condensation of tarry matter being heavy feedstocks, particularly hydrocarbon having a high boiling point are hastened due to free sulfur which is inevitably yielded in an instance by pyrolyzing sulfur compounds to form an extremely increased amount of coke. Even when such a reaction is carried out in a presence of hydrogen, such a harmful action of sulfur are not negligible. Inasmuch as metal complexes, free sulfur and H_2S are solidified upon a reaction on Ca-ion, the farmful action of the accelerated increase of the solid asphaltic fraction involved in petroleum refining is supressed due to metals such as vanadium and nickel and free sulfur, thereby to markedly increase the yield of refining distillate. In addition to an effect to improve petroleum refining products in quality due to CaO and $Ca(OH)_2$ because of condensed vanadium, nickel and sulfur in a solid segregated as a result of coprecipitation of CaO and $Ca(OH)_2$, the petroleum refining process according to the present invention entails a superior effect of heat treatment and thermal cracking by use of chemicals such as CaO and $Ca(OH)_2$. In this case, the reaction of CaO and $Ca(OH)_2$ necessitates coexistence of moisture, preferably steam. When adding 3 weight % of CaO to vacuum residue of Kuwait crude oil used as feedstocks, 36 weight % of coke is yielded at 460°C in a presence of no steam, whereas 28 weight % of coke is yielded in a presence of 2% steam, and 18 weight % of coke in a presence of 30% steam, and further, 16 weight % of coke in a presence of 50% steam. Thus, the yield of coke is remarkably reduced, and as a result, the amount of extracted oils increases with the reduced amount of coke, namely, by about 12% to 15%, and the majority of the components increased consists of kerosene and fraction of gas oil. In order to accomplish an incrased yield of extracted oil practicable in petroleum refining and solidification of metals and sulfur in coke, it is compulsory and important to use either water or steam, and the required amount thereof is at least three to eight times and at most ten to thirty times the amount of CaO and $Ca(OH)_2$. Even when only CaO and $Ca(OH)_2$ are mixed into the heavey feedstocks, no foamy effluence of the feedstocks occurs at the temperature in the range of from 200°C to 550°C; nevertheless, the feedstocks with such mixtures are foamed in a presence of steam. The degree of the foamy effluence depends on a kind of crude petroleum. For example, vacuum residue of Daqing crude petroleum gives rise to severe foamy effluence compared with atmospheric residue of Minus crude petroleum. This foamy effluence is caused by a strongly basic surface active agency of CaO and $Ca(OH)_2$ due to coexistence of water or steam. At any rate, water is compulsory. The surface active agency of CaO and $Ca(OH)_2$ is reduced in its viscosity and interfacial tension by mixing the heavy feedstocks of high viscosity with 1 to 3 % water. Despit vacuum residue of Daqing crude petroleum without an addition compound can be conveyed in 1.5 kg/min at 50°C through pipelines by use of a pump having a fixed horsepower, residue with 1 to 3 % CaO can be conveyed in 2.0 to 2.1 kg/min under the same condition thereby carrying out transportation of oil ecconomically.

In brief, the feature of the refining process according to the present invention is to maintain heavy feedstocks under the condition of strongly basic surface activation of Ca-ion at the temperature in the range of from 350°C to 550°C. The amount of gas yielded by subjecting heavy feedstocks with an addition compounds of CaO and $Ca(OH)_2$ to heat treatment at the temperature in the range of from 400°C to 550°C under coexistance of water or steam is somewhat more than that in case of feedstocks without addition compound. When vacuum residue of

Murban/Oman crude petroleum is treated at 530°C, 60 - 66 ℓ/kg of gas is produced with addition compound of 3% $Ca(OH)_2$, and however, 50 - 52 ℓ/kg of gas is yielded without addition compound. The components of the cracked gas are of 6 mol % of hydrogen with 3% addition compound, 8 mol % of hydrogen without addition compound; 29 mol % of methane with 3% addition compound, 25 mol % of methane without addition compound; 11.0 mol % of C_3 with 3% addition compound, 13.3 mol % of C_3 without addition compound. When vacuum residue of Daqing crude petroleum is treated at 530°C, 37 - 44 ℓ/kg of gas is yielded with addition compound of 3% $Ca(OH)_2$, and when it is treated at 490°C, 20 - 24 ℓ/kg of gas is yielded with addition compound of 1% $Ca(OH)_2$, and on the other hand, 16 - 23 ℓ/kg of gas is yielded without addition compound.

Particulary noteworthy is the fact that, in spite of cracked gas formation being somewhat increased, the amount of the formed coke is halved, and instead, the cracked distillate is certainly increased, and that gas oil fraction is more than gasoline fraction.

The component such as tar sand bitumen, which contains a high percentage of metals such as vanadium and nickel is so treated that it reacts upon Ca-ion to be turned into a solid in a separatably form from liquid oil together with solid asphaltic fraction.

The chemicals of strongly basic alkalin earth compounds such as CaO and $Ca(OH)_2$ to be used for heavy feedstocks at the temperature in the range of from 400°C to 550°C in the petroleum refining process according to the present invention has satisfactory property of strongly basic surface activation of Ca-ion at the temperature in the range of from 400°C to 550°C.

The most of the characteristic features of the present invention consists in an increased yield of gas oil fraction as refining distillate and a reduction of coke formation.

The present invention aims at a continuous increase yield of middle oil, particularly gas oil, from heavy feedstocks as raw material by use of chemicals such as CaO and $Ca(OH)_2$. But the increased yield of the middle oil is not accomplished only by desulfurization due to CaO and $Ca(OH)_2$ and solidification of metals such as vanadium and nickel. It is attained under coexistence of CaO and $Ca(OH)_2$ and water or steam and entails a large reduction of coke formation thus involved. The additional interest of the present invention lies in that the yield of gas is slightly increased. It is unexpected that the yield of gas is increased, despite that of coke is reduced. However, as a result of measurement of the composition of yielded gas, H_2 and C_3 - C_4 hydrocarbon are ascertained to be reduced and methane to be increased. If CaO and $Ca(OH)_2$ are not mixed, thermal cracking for taking measures to increase C_3 - C_4 gaseous hydrocarbon and gasolinic hydrocarbon is preferentially carried out. The thermal cracking is further promoted due to sulfur, metals and carbon. It is, however, anticipated that the thermal cracking being promoted due to sulfur, metals and carbon is suppressed when CaO and $Ca(OH)_2$ exist together, and in the meantime, the thermal cracking by which analysis is stopped is preferentially carried out when interrupted due to gas oil of high molecular weight and high boiling point. Essentially, heavy feedstocks of petroleum are not soiled by metals such as vanadium and nickel, sulfur, oxygen compounds and nitrogen compounds. Thus, from extremely pure heavy feedstocks, the yield of distillation fraction of middle oil, particularly gas oil is to be increased at the temperature in the range of from 400°C to 550°C. Solids of carboneus matters such as active carbon and soiled mesocarbon readily absorbs oxygen compounds on its surface and is soiled by metals, sulfur, oxygen compound and nitorgen compound, thereby reducing the yield of middle oil, particularly gas oil. This principle will be easily understood even from the fact that synthesizing zeolite is practically applied to catalytic cracking for gas oil. So far as a refining process carried out at the temperature in the range of from 400°C to 550°C by using chemicals such as CaO and $Ca(OH)_2$ makes use of a certain quantity of water or steam, even if any kind of heavy feedstocks is used as raw material, the most of raw material is soiled by metals such as vanadium and nickel, mud, ash, sulfur, oxygen, nitrogen and carboneus matter (asphaltene and soiled mesocarbon), thereby suppressing "unclear pyrolysis" thus involved which brings about an remarkable reduction in the yield of middle oil, particularly gas oil (on the basis of the art for positively promoting the pyrolysis by means of catalytic analaysis using zeolite). It can be considered that the principle contributes to keep pyrolysis of heavy feedstocks in a clear condition. And strongly basic surface activiation of Ca-ion at the temperature in the range of from 400°C to 550°C serves to remove various soiled impurities from the heavy feedstocks and solidify and segregate them.

The basic process according to the present invention is explained hereinafter.

Heavy feedstocks 1 are inhaled by a pump 4 and mixed with slurry of milk of lime discharged from a vessel 2 by means of a pump 3, and the mixture thus obtained is forwarded into a heater 6 via a heat exchanger 5 and heated in the heater 6 while constantly keeping the output temperature at the desired temperature in the range of from 400°C to 550°C. Thereafter, the mixture is fed into one of surge drums 7 and 8, thereby accumulating solid asphaltic fractions on the bottom of the surge drum. Two surge drums are alternatively used so that, where the yield of the solid asphaltic fractions collected in one of surge drums reaches a certain quantity, a supply of the feedstocks to the one surge drum is discontinued and at the same time, the feedstocks begins to be supplied to the other surge drum. After the rest surge drum is purged with steam to remove oil and gas collected therein, manhole covers disposed on the top and bottom of the rest surge drum are opened, and then, a hard solid body formed in the drum is quarried out by virtue of high pressure water being injected inside the drum through the upper manhole thereof by means of a water jet cutter and the solid asphaltic fractions 10 is discharged through the lower manhole. Each surge drum is provided on its lower portion with a steam blowing nozzle 9. Steam to be injected inside the surge drum from the nozzle 9 contributes to mixing sufficiently the heavy feedstocks fed into the surge drum with $Ca(OH)_2$ to maintain the condition of strongly basic surface activiation of Ca-ion at an arbitrary temperatures in the range of from 400°C to 550°C, and to accelerating the reaction to solidify metals, sulfur, etc. while minimizing solid asphaltic fractions. An oil inlet port may be disposed on any portion of the top, the side wall and the bottom of the surge drum. It is preferable to mount the oil inlet port between the top and the side wall thereof when the reaction temperature is relatively low. At any rate, a place at which the oil inlet port is determined by quality and quantity of solid asphaltic fractions subsided in and adhered to one of the surge drums 7 and 8. The time for which heavy feedstocks is stayed at the surge drum may be controlled on the basis of the amount of steam supplied. When a large amound of steam is supplied or a specific raw material is used, a foamed body yielded in the surge drum overflows and is fed into a distilling column 11 while solid asphaltic fractions and its precurson are fed thereinto. Then, a purpose to obtain a desired petroleum product by oil refining and a kind of raw materials enable determination on wheter solid asphaltic fractions is subjected to a segregation treatment in a settler 18 to obtain slurry-like fuel oil 20, or whether the feedstocks are to be recycled via a pipeline 21, in order to recover gas 14, gasoline 15 from the top of the distilling column 11, kerosine 16, gas oil 17 from the side portion thereof and clarified fuel oil 19 from the bottom thereof.

When unexpensive fuel for a gas turbine or Diesel engine is chiefly produced from tar sand bitumen, it is necessary to sufficiently remove metals such as vanadium, nickel, sodium and the like which are comprehended in large quantities by the bitumen therefrom. The heat treatment refining process carried out at the temperature in the range of from 400°C to 550°C to maintain the condition of strongly basic surface activiation of Ca-ion in the surge drum meets the aforesaid requirement. In this case, it is proper to keep the temperature in the range of from 400°C to 500°C.

At a lower temperature, the yields of gas and gasoline are reduced, and at a higher temperature, the yield of coke is increased though a faster reaction is caused. Also, when producing raw material used for productions of ethylene and prophlene adapted for petrochemistry from vacuum residue of Daqing crude petroleum and Minus crude petroleum, it is suitable to maintain the interior of the surge drum at a lower temperature, preferably in the range of from 400°C to 500°C so as to increase the yield of distillate such as middle oil and gas oil of good quality, which is adapted to reduce the yield of coke and gas. By selecting a lower temperature, the distillate of good quality being low in bromine value thereby entailing a reduced consumption of hydrogen can be yielded. Even when the superior distillate obtained by the present invention is applied to the conventional short-time staying type cracking furnace and subjected to a transfer line quench heat exchange in the hydrofining process which is performed while continuously adding contact hydrogen little by little, the coke formation does not exert a baneful influence upon the surfaces of the boiler tubes.

Further, it is desirable to collect middle oil of good quality (kerosine 16 and gas oil 17) from raw material for hydrocracking and FCC, therefore, recycling the majority of percipitate oil on the bottom of the distilling column through the pipeline 21 so as not to collect fuel oil 19. It may be attempted that the yield of the distillate thus obtained is increased so that gas oil having a high boiling point by returning settler 18 to a reboiler (combined with a second heater) and the fuel oil 19 to the distilling column 11.

EXAMPLE 1

Residual substance of atmospheric distillate (mixed Middle Eastern crude petroleum) of specific gravity of 0.9429 (15/4°C), 2.6 weight % of sulfur content, 5 g/100g of bromine value, and the composition (by elution chromatography) of 50.0% mixed paraffin and olefine hydrocarbons, 45.6% mixed aromatic hydrocarbon and diene synthesis, 1.6% resin and 2.8% the others, and showing initial boiling point (IBP) at 225°C, 10% at 340°C, 20% at 375°C, 30% at 470°C by ASTM distillation test was used as raw material. The raw material was fed into a pressure vessel at the temperature of from 450°C to 470°C and the pressure of 5kg/cm^2-gauge and subjected to a coking treatment for 20 hours with the result that a product consisting of 28.2 weight % of cracked gas, 25,2 weight % of mixed coke and cracked oil; whose distillate is of 36.4 weight % below 250°C, 10.2 weight % at 250 - 350°C, namely, 46.6 weight % of coked extract oil in all total were yielded. As to the properties of the products thus obtained, the distillate below 250°C is of specific gravity of 0.7756(15/4°C), and consists of 0.50 weight % of sulfur content, 17.7 weight % of aromatic hydrocarbon, 26.1 weight % of olefine hydrocabon, 56.1 weight % of saturation hydrocarbon, and shows IBP at 60°C, 10% at 108°C, 20% at 129°C, 50% at 175°C. 90% at 234°C, 95% at 246°C; whose distillation at the temperature in the range of from 250°C to 350°C is of specific gravity of 0.8509 (15/4°C) and average molecular weight of 200, 16 g/100g of bromine value, and consists of 1.47 wieght % of sulfur content; the coke thus yielded was of 4.5 weight % of sulfur content.

On the contrary, according to the present invention, coking treatment was carried out in the same condition as described above except that 3 weight % of calcium hydroxide having particle size less than 100 mesh, preferably 4 - 8 μm, is added in the form of water slurry to the raw material with the result that a product consisting of 13.3 weight % of cracked gas, 12.0 weight % of coke and cracked oil of 13.2 weight % distillation below 250°C, 22.3 weight % at 250°C to 350°C, 39.2 weight % above 350°C, namely, 74.7 weight % of coked distillation oil in all total was yielded. As to the properties of the products thus obtained, the distillation below 250°C is of specific gravity of 0.783 (15/4°C), and consists of 0.56 weight % of sulfur content, and the composition (by elution chromatograph) of 42.4% aromatic hydrocarbon, 4.8 % olefine hydrocarbon, 52.8% saturation hydrocarbon; whose distillation at 250°C - 350°C is of specific gravity of 0.871 (15/4°C) and 25.6 g/100g of bromine value, and consists of 1.63 weight % of sulfur content, and whose distillation above 350°C is of specific gravity of 0.941 (15/4°C) and 8 g/100g of bromine value and consists of 2.37 weight % of sulfur content; and coke was of 1.86 weight % of sulfur content.

EXAMPLE 2

In Tables 2, 3 and 4 are set out the results of experiments which were carried out by use of heavy feedstocks represented in Table 1 in conformity with the operating sequence illustrated in the accompanying flow sheet under such a condition that the surge drum is maintained at the temperature of from 490°C to 530°C to confirm the effect of addition of CaO having particle size less than 100 mesh, preferably 4 - 8 μm in its average size. As is evidenced from the following Tables, the addition of CaO contributes to increasing the yield of light oil (gas oil) by a large quantity and further to solidifying, within coke, sulfur contained by the feedstocks. As to the sulfur components, combustible sulfur is obtained by subjecting SO_2 which is obtained by burning the coke containing sulfur at 800°C, to a quantitation analysis, and solidified sulfur is obtained by subjecting SO_3 which is obtained by burning the coke at 1500°C, to a quantitation analysis. The sum content of the combustible sulfur and solidified sulfur is represented as 100 per cent, in Tables. Compared with the case in which CaO is used as addition compound, sulfur is appearently, remarkably solidified. This is extremely important for a refining process. When the yielded coke is burnt to be gasfied or used as fuel, it does not generate sulfur compounds at the temperature below 800°C, and thereby gas thus exhausted is clean. As in Boscan crude petroleum, vanadium contained therein is solidified within coke and it is almost remained in heavy oil. On the contrary, when no addition compound is used, vanadium is almost remained in heavy oil. Thus, it is extremely important for a refining process to effectively solidify vanadium within coke, but not remain heavy oil, thereby allowing the heavy oil to be adopted as fuel for a gas turbine and a Diesel engine. It is worth noting that light oil and heavy oil obtained by novel refining process according to the present invention do not cause a lowering of active power thereof even when the conventional catalyst is used, and consequently, the process of the present invention can substitute for the conventional process in which hydrogen and troublesome catalyst are used for a preliminary process for treating super heavy quality oil such as tar sand bitumen.

EXAMPLE 1

Table 1 : Properties of Heavy Feedstocks

	Murban/Oman vacuum residue	Boscan crude	Daqing vacuum residue
Specific gravity (15/4°C)	0.979	0.999	0.947
Pour point (°C)	+27.5	-	+32.5
Conradson carbon residue (wt %)	13.8	16.2	8.6
Ash content (wt %)	0.02	0.24	-
Sulfur content (wt %)	2.27	5.28	0.18
Nitrogen content (wt %)	0.24	0.54	0.37
Composition analysis (wt %)			
Saturation content	37.1	29.3	42.7
Aromatic content	43.3	39.1	31.3
Resin content	17.5	19.1	25.7
Asphaltene content	2.1	12.5	0.3
Metal analysis (ppm)			
Na	31	24	9
Ni	23	114	9
V	30	1221	<1
Fe	-	9	-
Ca	-	7	-

Table 2 : Properties by Murban/Oman crude vacuum residue

Presence of addition	3 wt% of CaO	No addition
Temperature in surge drum (°C)	530	530
Yield (wt %):		
H_2, C_1 - C_6 Distillation (°C)	8.0	7.4
Coker naphtha (C_7 - 205°C)	9.7	9.2
Light oil (250-400°C)	71.7	61.4
Coke	10.6	22.0
Properties:		
Coker naphtha:		
Specific gravity (15/4°C)	0.732	0.734
Sulfur (wt %)	0.34	0.44
Light oil:		
Specific gravity (15/4°C)	0.840	0.839
Sulfur (wt %)	1.54	1.59
Coke:		
Sulfur (wt %)	3.75	3.68
Calorific value (cal/g)	7470	8190
Combustible sulfur (800°C)	25%	96%
Solidified sulfur (800°C)	75%	4%

Table 3 : Properties by Daqing crude vacuum residue

Presence of addition	1 wt % of $Ca(OH)_2$	No addition
Temperature in surge drum (°C)	490	490
Yield (wt %):		
H_2, C_1 - C_6 distillation (°C)	7.0	6.5
Coker naphtha (C_7 - 205°C)	17.7	18.0
Light oil (205-400°C)	63.0	58.3
Coke	9.3	14.0
Loss	3.0	3.2
Properties:		
Coker naphtha:		
Specific gravity (15/4°C)	0.742	0.743
Sulfur (wt %)	0.01	0.04
Light oil:		
Specific gravity (15/4°C)	0.829	0.820
Sulfur (wt %)	0.09	0.11
Coke:		
Sulfur (wt %)	0.80	0.45
Calorific value (cal/g)	8009	9500
Combustible sulfur (800°C)	3%	82%
Solidified sulfur (800°C)	97%	18%

Table 4 : Properties by Boscan crude vacuum residue

Presence of addition	3 wt % of CaO	No addition
Temperature in surge drum (°C)	490	490
Yield (wt %):		
H_2, C_1 - C_6 distillation(°C)	8.0	7.7
Coker naphtha (C_7 - 205°C)	17.5	14.6
Light oil (250-400°C)	49.0	39.3
Heavy oil (> 350°C)	6.5	12.6
Coke	17.4	23.8
Loss	1.6	2.0
Properties:		
Coker naphtha:		
Specific gravity (15/4°C)	0.742	0.745
Sulfur (wt %)	0.35	0.48
Light oil:		
Specific gravity (15/4°C)	0.857	0.876
Sulfur (wt %)	3.08	3.22
Heavy oil:		
Specific gravity (15/4°C)	0.923	0.944
Sulfur (wt %)	3.68	3.89
Vanadium (ppm)	1	50
Coke:		
Sulfur (wt %)	8.51	8.80
Calorific value (cal/g)	8326	9109
Combustible sulfur (800°C)	18.9%	98.2%
Solidified sulfur (800°C)	81.1%	1.8%
Vanadium	1.13%	0.80%

WHAT IS CLAIMED IS:

1. A refining process for petroleum and the like in pyrolysis for heavy feedstocks thereof, which comprises supplying to the pipeline of a heating furnace the feedstocks mixed with oxide of alkaline earth metal, or hydroxide content and water respectively, or the mixture thereof with slurry-like addition compound to be heated; staying the heated feedstocks at a soaking drum for 1 second to 30 minutes after the heating temperature reaches to the range of from 350°C to 550°C and a pressure gauge reaches about 1 to 20 kg/cm^2; and continuously segregating gas and residue from the feedstocks at a distilling column while precipitating and solidifying asphaltene, heavy metals and sulfur content to segregate them as solid bodies therefrom by maintaining the condition of strongly basic surface activiation of Ca-ion.

2. The refining process according to Claim 1, wherein the yield of distilled oil of good quality, particularly gas oil, is increased.

3. The refining process according to Claim 1, wherein heavy oils of good quality for gas turbine and Diesel engine, which contain a small amount of heavy metal content such as vanadium and nickel under the condition of the output temperature of the heating furnace in the range of from 350°C to 500°C and for the staying period from 1 second to 30 minutes in the socking drum.

4. The refining process according to Claim 1, wherein distillation of the feedstocks for petrochemistry is yielded under the condition of the output temperature of the heating furnace in the range of from 400°C to 500°C and for the staying period from 1 second to 10 minutes in the soaking drum.

5. The refining process according to Claim 1, wherein feedstocks for FCC and hydrocracking of good quality are yielded under the condition of the output temperature of the heating furnace in the range of from 400°C to 550°C and for the staying period from 1 second to 10 minutes in the soaking drum.

6. The refining process according to Claim 1, wherein the oxide of alkaline earth metal is CaO.

7. The refining process according to Claim 1, wherein the hydroxide of alkaline earth metal is $Ca(OH)_2$.

8. The refining process according to Claim 1, wherein a delayed coking drum is used as the soaking drum, thereby to increase the yield of middle oil.

9. The refining process according to Claim 1, wherein a fluid coking drum is used as the soaking drum thereby to increase the yield of middle oil.

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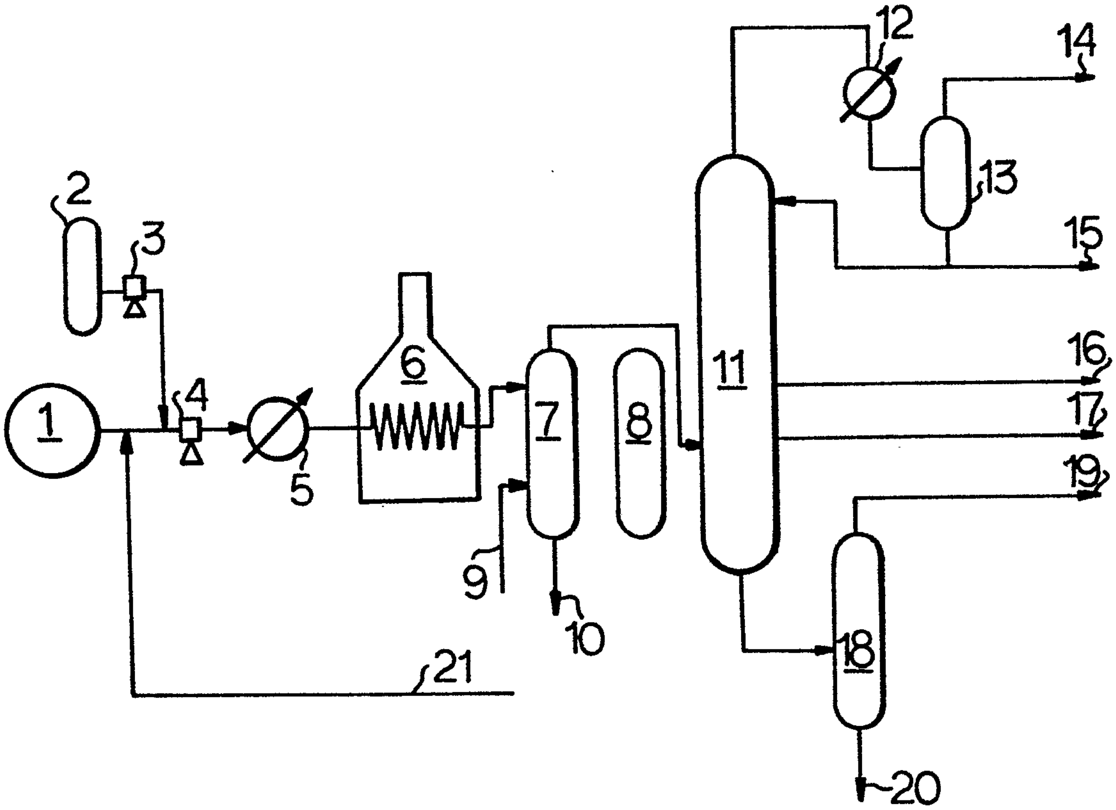

European Patent Office

EUROPEAN SEARCH REPORT

0072873

Application number

EP 81106517.6

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
A	GB - A - 1 576 720 (STANDARD OIL COMPANY) * Claims 1-3,12,13; page 2, lines 50-65; page 3, lines 1 - page 5, line 15 * --	1-9
A	GB - A - 1 307 543 (ESSO RESEARCH AND ENGINEERING COMPANY) * Claims 1-9; page 1, line 86 - page 2, line 9 * --	1-9
A	US - A - 3 707 462 (G.MOSS) * Claim 1; column 1, line 22 - column 2, line 32 * --	1-9
A	US - A - 3 707 459 (R.B.MASON et al) * Claims 1,3; column 1, line 65 - column 2, line 28; column 3, lines 38-47 * ----	1-9

CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)

C 10 G 11/04
C 10 G 19/00

TECHNICAL FIELDS SEARCHED (Int.Cl. 3)

C 10 G

CATEGORY OF CITED DOCUMENTS

X: particularly relevant if taken alone
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A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: earlier patent document, but published on, or after the filing date
D: document cited in the application
L: document cited for other reasons

&: member of the same patent family, corresponding document

X The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	31-03-1982	STÖCKLMAYER

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