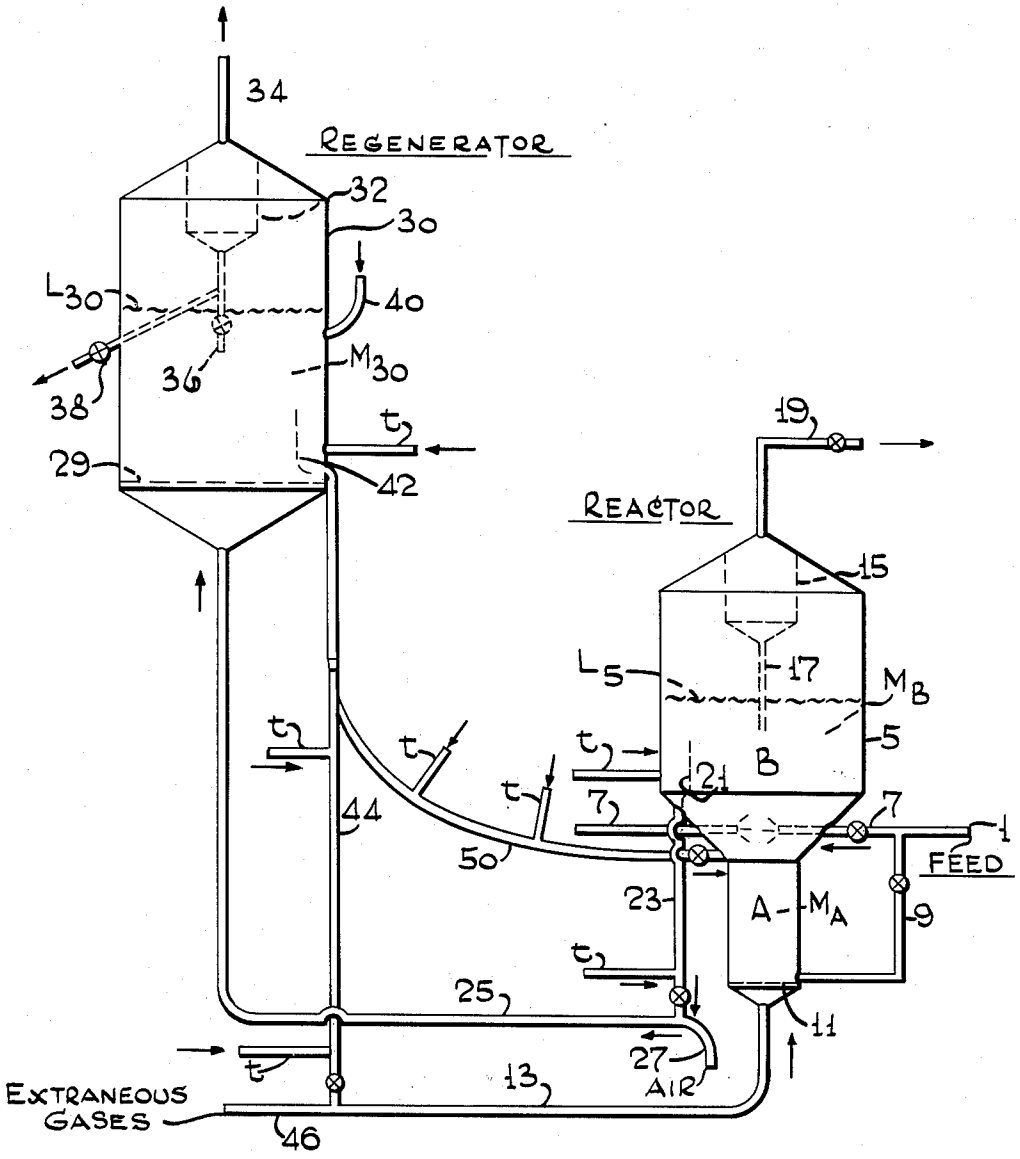
Jan. 24, 1956 R. W. KREBS ET AL 2,732,330

CONVERSION OF HYDROCARBON OILS WITH THE USE OF FLUIDIZED SOLID PARTICLES

Filed Oct. 31, 1950



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United States Patent Office 2,732,330 Patented Jan. 24, 1956

2,732,330

CONVERSION OF HYDROCARBON OILS WITH THE USE OF FLUIDIZED SOLID PARTICLES

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Application October 31, 1950, Serial No. 193,062

6 Claims. (Cl. 196—52)

The present invention relates to a method and apparatus for treating hydrocarbon oils. More particularly, the invention pertains to the production of gasoline as well as higher boiling distillate fractions from heavy hydrocarbon oils of the type of topped or reduced crude or similar heavy residues. In its broadest aspect the invention provides for contacting heavy residues of the type mentioned with hot subdivided fluidized solids at temperatures conducive to the coking and cracking of the residues and producing the vapors and gases required for fluidization by pre-cracking a portion of the residue feed.

In refining crude oil it is standard practice first to subject the crude to simple distillation or "topping" to produce various distillate fractions, such as naphtha, heating oil and gas oil cuts boiling up to about 800°–950° F. Most of these distillate fractions are normally converted into high quality gasoline range motor fuels by such conventional treatments as thermal and/or catalytic reforming and cracking, or similar operations.

The residue from the crude distillation may be processed to yield valuable high molecular weight materials including lubricating oils, waxes, resins, fuel oils, asphalt, etc. depending on the origin and character of the crude. More recently, however, the demand for motor fuels has increased so greatly that it has become extremely difficult to satisfy the motor fuel market by merely processing crude distillates in the manner indicated above. This situation has prompted considerable research and development work directed toward an efficient conversion of crude residua into additional quantities of motor fuels. The two most common methods used for this purpose in current practice are viscosity-breaking and coking of reduced crude.

Viscosity-breaking involves a treatment of reduced crude or the like at elevated temperatures for a short period of time adequate for the formation of an additional quantity of gas oil and about 5–15% of gasoline. The gas oil forms a suitable feed stock for thermal or catalytic cracking and may be converted into gasoline in this manner. However, extensive cracking facilities in addition to the crude still and vis-breaking units are indispensable for the production of satisfactory quantities of gasoline by vis-breaking of reduced crude.

The other method, i. e., coking of reduced crude, is a much more drastic heat treatment usually carried out at higher temperatures, of say, about 800°–1000° F. and for longer times. It results in direct production of increased proportions of gasoline of, say, about 15–35% in addition to gas oil and hydrocarbon gases together with solid coke. This process lends itself more readily than vis-breaking to the purpose of producing maximum amounts of gasoline from reduced crude in the most economical manner, particularly in view of the fact that sufficient coke is produced to supply by combustion the heat requirements of the process. Therefore, the research efforts of the industry most recently have concentrated on improvements of this type of operation.

Broadly, the present invention is concerned with such improvements.

One of the major difficulties complicating a successful coking operation results from the heavy deposition of coke in the coking vessels and transfer lines requiring frequent and time-consuming cleaning periods. This problem has been solved or at least greatly alleviated, prior to the present invention, by admixing with the residuum to be coked substantial proportions of a subdivided inert adsorbent solid, such as petroleum or other coke, pumice, kieselguhr, spent clay, sand, or the like, which serves primarily as a carrier for the coke formed so as to prevent coke deposition on equipment walls and also as a scouring agent removing coke deposits from the walls. The high surface area provided by these solids in some cases as, for example, with spent clay, also accelerates and intensifies the cracking reaction whereby larger yields of gasoline within short holding times may be obtained without any danger of deactivation of the solids by carbon deposits or ash constituents of the feed. The coke deposited on the solids may be burnt off in cyclic or continuous two-vessel operation to generate and supply to the coking vessel the heat required for coking.

While fixed bed and suspensoid systems have been suggested for this type of operation, the so-called fluid solids technique offers greatest advantages with respect to temperature control, heat economy, ease and continuity of operation and equipment dimensions. This technique in its application to the coking of reduced crude involves the injection of the feed into a relatively dense highly turbulent bed of hot subdivided solids having a particle size of about 30–400 mesh, fluidized by a gas flowing upwardly through the bed at a linear superficial velocity of about 0.2–3 ft. per second to give the bed the appearance of a boiling liquid separated by a definite interface from an upper dilute suspension of solids in gases and gasiform products. Volatile coking products are removed overhead and further treated after the removal of entrained solids. In some of the adaptations of the process, coke carrying solids are continuously passed to a fluid type combustion zone wherein they are fluidized by a combustion-supporting gas and coke is burnt off to heat the solids to a temperature higher than coking temperature. Hot solids are continuously recirculated to the coking zone in amounts sufficient to supply most of the heat required therein.

While this procedure affords excellent heat control and utilization as well as better yields of desirable products as compared to other systems, certain difficulties arise in connection with the fluidization of the heat carrying solids. It is necessary to fluidize these solids before the heavy residue feed is introduced into the reactor. For this purpose, steam or inert gas, such as fluegas or recirculated process gas have been proposed in the past. Substantial amounts of these extraneous fluidizing gases are required, particularly when operating at relatively low temperatures of, say, less than 1100° F. which have been found to be highly beneficial for establishing a desirable product distribution in the effluent of the coking zone. For example, expedimental data indicate that in cracking vacuum residua over inert solids at temperatures below 1000° F., more than 35 wt. per cent of steam based on residue charged is required to prevent excessive coke deposition and loss of fluidization. Even at temperatures as high as 1100° F. the minimum fluidizing steam requirement is about 10–20 wt. per cent. The provision of fluidizing gases in these proportions adds considerably to the cost of the cracking process. The present invention substantally alleviates this difficulty.

It is, therefore, the principal object of the present invention to provide an improved fluid-type process and

apparatus for coking and cracking crude residua or similar materials wherein the amount of extraneous fluidizing gas required may be substantially reduced. Other and more specific objects and advantages will appear from the description below wherein reference will be made to the accompanying drawing, the single figure of which is a semi-diagrammatic illustration of a system adapted to carry out a preferred embodiment of the invention.

In accordance with the present invention, at least a substantial proportion and preferably at least a major proportion of the fluidizing gas required for the fluidization of hot solids contacted with the heavy residue to be coked is produced by gasifying a minor proportion of the residue feed. For this purpose, a minor proportion of the residue feed is contacted with a narrowly confined, i. e., small diameter, dense, fluidized bed of hot solids at conditions conducive to substantially complete gasification by vaporization and cracking, of all gasifiable constituents of said minor feed proportion. The vapors and gases so produced are passed upwardly through an expanded, i. e. large diameter, dense fluidized bed of hot solids superimposed on, and in direct contact with, said confined bed in such a manner that the gases leaving the confiined bed properly fluidize the expanded bed. The remainder of the residue feed is fed directly to the upper expanded bed. Proper fluidization of the lower confined bed, particularly in its lower portions may be accomplished by supplying a relatively small amount of an extraneous fluidizing gas, such as steam or recycle gas to the bottom portion of the confined bed. Because of the small diameter of this confined bed the total amount of extraneous fluidizing gas required for proper fluidization of this bed is substantially smaller than that which would be required to fluidize a solids bed of uniform diameter but sufficient hold-up to coke and crack the entire feed supplied thereto in a single stream. When operating in this manner, proper fluidization may be accomplished without the requirement of excessive amounts of extraneous fluidizing gas, such as steam, even when operating at relatively low temperatures of, say, about 850°–1050° F. The invention, therefore, has particular utility in connection with this type of low temperature operation.

In accordance with the preferred embodiment of the present invention, solids heated in a fluid-type combustion zone to a temperature above the desired coking and cracking temperature, say to a temperature of about 900°–1200° F., are first contacted with about 5–30% of the heavy residue feed stock in a lower constricted portion of a fluidized solids bed so as to accomplish substantially complete gasification and coking of the feed therein. A small amount of steam or other fluidizing gas may be fed to this portion of the fluid bed to establish a proper fluidizing gas velocity of about 1–10 ft. per second. The temperature in the constricted portion should be relatively high, say about 1000°–1150° F. and the feed residence time about 1 to 5 seconds when calculated as a vapor. The upper expanded portion of the fluidized bed may be maintained at the desired relatively low coking and cracking temperature of about 850°–1050° F., the gaseous effluent of the lower zone serving to fluidize the upper portion of the bed so that the remainder of the residue feed may be supplied thereto without the danger of fluidization troubles. Substantially larger vapor residence times of, say, about 5–60 seconds are provided in the upper portion of the fluidized bed. The treating temperatures mentioned may be readily maintained by continuously passing highly heated solids from the combustion zone to a lower portion of the constricted bed and from there into the expanded portion of the bed. However, a substantial, and in many cases even a major portion, of the total hot solids required for this purpose may be directly supplied from the combustion zone to a lower portion of the upper expanded portion of the fluidized bed. The relative dimensions of the two beds of different diameter should be such that the amount of extraneous gas added to the constricted zone plus the gas produced therein by cracking and vaporization are sufficient to establish a proper fluidization velocity of about 0.2–3 ft. per second in the upper expanded bed. The solids used for the purposes of the invention may be either inert, such as petroleum coke, sand, pumice, etc., or catalytic, such as activated clays, synthetic silica-alumina or silica magnesia composites, and the like.

The advantage secured by this type of operation is highly significant. For example, a process may normally require 10 wt. percent of steam for proper fluidization in a reaction vessel of uniform diameter. The average molecular weight of the products of complete gasification of the feed may be of the order of 15 to 45. A typical figure often used in calculations is 28. The total fluidizing gas requirement may, therefore, be supplied by subjecting merely 16% of the residuum feed to complete gasification in accordance with the invention. This percentage may be calculated by applying the ratio of molecular weights to the percentage of steam which would otherwise be used, e. g.

$$10\times\frac{28}{18}=16\%$$

Having described its objects and general nature, the invention will be best understood from the more detailed description hereinafter in which reference will be made to the accompanying drawing.

Referring now to the drawing, the system illustrated therein essentially comprises a reactor 5 and a heater 30, the functions and coaction of which will be presently described using the coking and cracking of a 2.4% South Louisiana residuum as an example. It should be understood, however, that the system may be employed to a similar treatment of other feed stocks in a generally analogous manner. While heater 30 is of conventional cylindrical design suitable for fluid-type dense phase draw-off operation, reactor 5 consists of a small-diameter lower cylindrical section A and a cylindrical large-diameter upper section B. The ratio of the diameters of sections A and B may be about 0.1 to 0.4 and the ratio of the heights of sections A and B about 0.3 to 1.

In operation, the reduced crude is supplied to the system from line 1 essentially in the liquid state at a temperature of about 500°–800° F. The feed is divided into two portions. A major proportion of, say, about 80 to 95% is supplied directly to a lower portion of section B of reactor 5, preferably by means of suitable spraying devices, via manifold lines 7. The remainder of the feed is supplied via line 9 in a similar manner to a lower portion of section A of reactor 5 at a point above distributing means such as perforated plate or grid 11 arranged in the bottom of section A. Simultaneously, highly heated solids such as coke, sand or a contact clay, having a fluidizable particle size of about 30–400 mesh, suspended in a fluidizing gas such as steam are supplied from line 13 through grid 11 at a temperature of about 1100°–1500° F., preferably about 1200°–1300° F., as will appear more clearly hereinafter. About 0.1 to 0.3 parts of steam and about 5 to 20 parts of solids supplied through line 13 per part of the total reduced crude feed supplied to section A are normally adequate for the purposes of the invention.

The hot solids entering section A through grid 11 are first contacted in section A with the minor feed portion supplied through line 9. As a result of the relatively high temperature of the solids and the relatively high solids: feed ratio in secion A, the liquid feed is immediately vaporized and extensively cracked in section A so that a highly turbulent fluidized solids mass M_A is formed therein having an apparent density of about 10 to 30 lbs. per cu. ft. and providing for a vapor residence

time of about 1 to 5 seconds. For the type and particle size of the solids here involved, the dimension of section A may be chosen to establish linear superficial vapor velocities in mass M_A of about 1 to 10 ft. per second. Heat is absorbed in section A by the vaporization and cracking reaction with the effect that the temperature of mass M_A is fairly uniform at about 1050°–1150° F.

Under the influence of the continuous feed of hot solids to the bottom of section A, fluidized solids flow upwardly into section B. Immediately upon entering section B, substantially at the temperature of mass M_A the solids are contacted with the major portion of the reduced crude feed supplied through manifold **7**. Thereupon vaporization, coking and cracking takes place. Additional vapors and gases are formed and coke is deposited on the solids. However, in spite of the increased amounts of gases and vapors present in zone B, their linear superficial velocity is maintained within a range of about 0.3 to 2 ft. per second, suitable for fluidization so that a dense turbulent mass M_B having an apparent density of about 20 to 60 lbs. per cu. ft. and a definite upper interface L_5 is formed within section B above mass M_A. As a result of the endothermic reactions taking place in mass M_B, the temperature of the latter may be readily maintained at the desirable lower level of about 850°–1000° F. The hold-up of mass M_B may be such as will provide for a vapor residence time of about 5 to 60 sec. therein. In this manner, proper fluidization is assured even at the relatively low temperatures of mass M_B while using only about 10% of the amount of steam which would be required for proper fluidization of mass M_B in the absence of the small diameter lower section A.

A mixture of gasiform reaction products and steam containing about 0.001 to 0.02 lbs. per cu. ft. of suspended solids fines flows overhead from interface L_5 and may be subjected to gas-solids separation in any suitable equipment, such as a cyclone separator **15**. Separated solids fines may be returned to mass M_B via dip-pipe **17**. Product vapors and gases now substantially free of entrained solids may be passed via line **19** to conventional product recovery equipment (not shown).

Fluidized solids carrying coke deposited at a rate of about 5 to 25 lbs. per 100 lbs. of residium fed may be withdrawn from well **21** through standpipe **23**, stripped and aerated with small amounts of a suitable gas, such as air, flue gas, steam, etc., supplied through taps *t* in a manner known per se. The withdrawn solids may be passed from standpipe **23** into line **25** at a rate similar to that of the solids supply via line **13**. Line **25** receives a combustion-supporting gas, such as air and/or oxygen, from line **27** in amounts adequate to permit the removal of about 0.5 to 3.0% of coke from the solids by combustion. About 140 to 200 standard cu. ft. of air per pound of carbon are normally suitable for this purpose. The relatively dilute suspension of solids-in-air or the like may be passed from line **25** through a distributing device **29** similar to grid **11** into the lower portion of heater **30** to form therein a dense fluidized mass M_{30} similar in appearance and behavior to mass M_B. Combustion of coke taking place in heater **30** is so controlled that the solids in mass M_{30} are reheated to a temperature of about 1100°–1500° F. which should be at least 50° F. higher than the temperature of mass M_A. Flue gases containing entrained solids fines and flowing overhead from level L_{30} may be passed through gas-solids separator **32** and thence via line **34** to any desired purpose. Separated solids may be returned to mass M_{30} via dip-pipe **36** or discarded via line **38**. The fluidized solid which is preferably used in the process is coke. Under the usual conditions, more coke is produced in the reaction vessel than is needed to supply the heat for the process through combustion in heater **30**. The excess coke is withdrawn through line **38** and may then be used for any desired purpose. In the event that an extraneous solid, such as a clay or sand, is used, it is often advantageous to withdraw a stream of that material bearing an appreciable amount of carbon so that it may be regenerated or burned in outside equipment both for recovery of the solid and the potential heat in the carbon. Make-up solids may be added via line **40**.

Fluidized solids may be withdrawn from heater **30** at the temperature of mass M_{30} through well **42** and standpipe **44** aerated and/or stripped with steam or inert gas via taps *t*. The reheated solids pass from standpipe **44** into line **13** wherein they are picked up by fluidizing gas, particularly steam supplied through line **46**, to be fed to section A of reactor **5** as described above.

When catalysts, such as activated clay or a synthetic silica-alumina, are used in place of, or in addition to, the inert solids referred to above, care should be taken to avoid catalyst deactivation by overheating the same in the carbon-burning state. This may be accomplished by maintaining the heater temperature at a level not substantially exceeding 1200° F. or at an even lower temperature. The reduction in temperature may be compensated for by increasing the catalyst circulation rate, thus keeping the quantity of heat transferred substantially constant. When it is desired to supply a portion, for example, say, 50–90% of the solids reheated in heater **30** directly to the upper expanded section B of reactor **5** this may be accomplished by means of line **50** leading into the bottom of section B. Other modifications within the spirit of the invention may appear to those skilled in the art.

The invention will be further illustrated by the following specific example.

Example

A 10° API vacuum pipe still bottoms may be cracked in a two zone vessel, as shown diagrammatically in the figure on coke having an average particle size of about 150 mesh, additional hot fluidized coke being introduced from heater vessel **30** via line **50** to the inlet of section B of reactor vessel **5** using the vessel dimensions and reaction conditions tabulated below.

	Section A	Section B
Pitch Rate, B/D	1,000	9,000
Reactor Vessel Diameter, Ft	4.5	15
Bed Height, Ft	12	20
Pressure, Lb./Sq. In. Ga	30	25
Fluid Bed Density, Lb./Cu. Ft	20	50
Pitch Weight Space Velocity, Lb./Hr./Lb	3.6	0.7
Fluid Coke Feed Rate, Lb./Min	2,310	11,550
Avg. Temperature of Coke entering Bed, ° F	1,150	1,140
Temperature of Bed, ° F	1,100	1,040
Coke/Oil Feed Ratio	10	5.6
Wt. Percent Steam on Feed	5	0.5
Superficial Velocity of total gases at inlet, Ft./Sec.	5.9	0.5

At the above conditions good fluidization is obtained in the main reaction zone B with the use of only 0.5% steam on feed, fluidization being accomplished mainly by the action of the cracked products from the lower reaction zone A.

The above description and exemplary operations have served to illustrate specific embodiments of the invention but are not intended to be limiting in scope.

What is claimed is:

1. In the process of producing distillate fractions from heavy residual hydrocarbon oils by contacting heavy residual hydrocarbon oil at coking conditions with a dense turbulent mass of subdivided hot solids fluidized by an upwardly flowing gasiform medium, the improvement which comprises introducing an original gasiform medium, which is only a minor part of the total fluidizing medium required, into the bottom of the dense turbulent mass, supplementing said medium by producing a major proportion of said gasiform medium requirements by contacting a minor proportion of liquid heavy residual hydrocarbon oil for a relatively short time with a narrowly confined fluidized mass of said hot solids maintained at

a relatively high coking temperature and fluidized at a relatively high linear gas velocity, said minor proportion of liquid being introduced above the bottom of said mass and separately from the original gasiform medium so as to coke and gasify said minor proportion substantially completely within said short time, passing gases so produced into a laterally expanded second mass of hot solids superimposed on and in direct contact with said first named mass, the two masses constituting a single uninterrupted fluidized bed, so as to fluidize said second mass at a relatively low linear gas velocity, supplying a major proportion of the heavy residual hydrocarbon oil directly to said second mass, contacting said major oil proportion with said second mass for a relatively long time sufficient for converting said major oil proportion into distillate oils and coke, recovering distillate oils overhead from the fluidized bed, passing coke-carrying solids from said bed to a combustion zone, burning coke off said coke-carrying solids in said combustion zone to reheat said solids to a temperature substantially higher than said relatively high coking temperature and returning at least a portion of the solids so reheated to said first named mass to supply said hot solids thereto.

2. The process of claim 1 in which a portion of said reheated solids is passed directly to said second mass.

3. The process of claim 1 in which the feed ratio of solids to oil in said first named mass is substantially greater than the feed ratio of solids to oil in said second mass.

4. In the process of producing distillate hydrocarbon fractions and coke from heavy hydrocarbon oil by contacting said oil at a coking temperature range of about 850° to 1050° F., with a mobile mass of non-catalytic preheated solids of fluidizable particle sizes, the improvement which comprises very substantially reducing inert fluidizing gas requirements by establishing a fluidized bed of said solids of narrow cross-section in its lower portion and broader cross-section in its upper portion, introducing at the bottom of said bed a relatively small stream of extraneous inert gasiform fluidizing medium which is sufficient to start fluidizing the bed at its narrow bottom part but inadequate to fluidize it at a broader higher level, introducing in liquid state part of the heavy oil to be coked into the narrow lower portion above the bottom and separately from the inert gasiform medium, continuously supplying hot solids to the lower portion to vaporize and crack the oil so fed and to provide vapors for substantially supplementing the bed-fluidizing action of the inert gasiform medium, and introducing a further part of the heavy oil as a liquid spray directly to the broader upper portion of the bed for conversion to distillate and coke.

5. Process according to claim 4 wherein the solid particles are predominantly coke particles produced in the process.

6. Process according to claim 4 wherein part of the coke produced is withdrawn from the system as product and part is reheated and returned to the fluidized bed for continuing the process.

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