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<p>(21) International Application No.: PCT/FR97/01630</p> <p>(22) Date of International Filing: 16 September 1997 (16.09.97)</p> <p>(30) Data relating to priority: 96/11379 18 September 1996 (18.09.96) FR</p> <p>(71) Filer (for all states designated with the exception of US): INSTITUT FRANÇAIS DU PETROLE [FR/FR]; 4, avenue de Bois Préau, F-92506 Rueil Malmaison (FR).</p> <p>(72) Inventors; and (75) Inventors/Filers (US only) PONTIER, Renaud [FR/FR], Le Village, Luzinay, F-38200 Vienne (FR); BONIFAY, Régis [FR/FR]; 10, rue de l'Alma, F-92600 Asnières (FR); COURTEHEUSE, Gérard [FR/FR]; 34, rue Camille Corot, F-925100 Rueil-Malmaison (FR); DEL POZO, Mariano [FR/FR], 43, rue Jules Siegfried, F-76600 Le Havre (FR); GAUTHIER, Thierry [FR/FR], 13, allée des Muses, F-69230 Saint Genis Laval (FR).</p> <p>(74) Representative: ANDREEFF, François, Institut Français du Pétrole, 4, avenue de Bois Préau, F-92506 Rueil Malmaison (FR).</p>	<p>(81) Designated States: CA, CN, JP, KR, MX, SG, US, European Patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</p> <p>Published <i>With International Search Report.</i></p>	
<p>(54) Title: METHOD AND DEVICE FOR DESCENDING CATALYTIC CRACKING BY INJECTING FEED AT AN ADEQUATE ANGLE ON A CONDITIONED CATALYST</p> <p>(57) Abstract:</p> <p>A process is described for the catalytic cracking of a petroleum feed, wherein the catalyst coming from a regeneration zone (4) is caused to flow in a conditioning zone (2) in dense fluidised bed upstream of an injection zone (10), the fluidisation rate being between 0.1 and 30 cm/s. A catalyst flow through a member with a constriction (11) is regulated in the injection zone (10), the hydrocarbon feed (12) below the member with the constriction is injected counter-current to the direction of flow of the catalyst shaped and at a predetermined injection angle as a function of the linear momentum of the feed and of the catalyst.</p>		

A PROCESS AND APPARATUS FOR DROPPER CATALYTIC CRACKING
INJECTING A FEED AT A SUITABLE ANGLE
ONTO A CONDITIONED CATALYST

The invention is concerned with a process for the fluidised bed catalytic cracking (FCC) of a hydrocarbon feed in a reaction zone where the feed flows from top to bottom (dropper).

One of the major problems encountered by the refiner is that of optimising the production of gasoline along with increased production of light C_3 olefins. Technological modifications to riser FCC units consist in reducing the residence time of the feed in the catalytic zone in order to bring such values to less than 0.5 s, essentially by increasing the circulation rate of the feed and catalyst. Combined with an increase in the reaction temperature, such a reduction in the residence time encourages primary cracking reactions which are to the detriment of consecutive hydrogen transfer and secondary cracking reactions.

In a further technological modification along the same lines, the back-mixing phenomenon which is characteristic of riser units is reduced by employing descending co-current flow of the gas and catalyst. In this type of flow, the radial concentration and flow rate profiles are "flatter", and so approach "piston" flow which is well-known in promoting gasoline selectivity and in reducing secondary cracking reactions.

The major problem with this type of reactor is concerned with the close contact between the hot regenerated catalyst and the hydrocarbon feed.

US Patent 4919898 describes the formation of a falling curtain of catalyst from rectangular openings coming from a bed pressurised by steam. This bed therefore controls the pressure difference between the vessel which contains the pressurised bed and a chamber for mixing the catalyst and the feed downstream of the bed.

This patent also describes the injection of the feed in the direction of the valve which forms the curtain.

Operating a pressurisation system on an industrial scale with a view to regulating flow rate is extremely difficult because there is a very large variation in flow rate for a very small pressure variation, which can result in an unstable solid flow rate which can therefore be deleterious to the selectivity of the desired products.

US Patent 5296131 also describes a downward flowing annular catalyst curtain. The feed is injected downwardly at least partly through a radial opening under the seat of a frustoconical plug valve which is placed against the upper part of the reactor.

The prior art is also illustrated by Patent Application EP-A-0 209 442 which describes the presence of a valve downstream of a first fluidisation ring which disturbs the fluidisation conditions until defluidisation occurs to produce a volumetric mass equal to a bulk bed.

The aim of the invention is to overcome the drawbacks of the prior art.

It has been noted that by conditioning the density of the catalyst by causing it to move in suitable geometric forms and by optimising the zone for injection of the feed into the reaction zone, the selectivity of the cracking reaction would be substantially improved.

To be more exact, the invention is concerned with a process for the fluidised bed catalytic cracking of a petroleum feed into lighter effluents in a catalytic cracking zone comprising a reaction zone, or dropper, into an upper end of which, termed the injection zone, regenerated catalyst coming from at least one regeneration zone is introduced, the catalyst is shaped by means of a shaping member having a constriction, the catalyst is contacted with the feed, a downward flowing mixture of catalyst and feed is formed, at least the majority of the feed is vaporised in said injection zone, said feed is cracked in order to obtain lighter effluents, the effluents

are separated from the spent catalyst in a separation zone at the lower end, the effluents are recovered, and the spent catalyst is recycled to the regeneration zone, the process being characterised in that the regenerated catalyst coming from the regeneration zone is caused to flow into a zone for conditioning the dense fluidised bed catalyst upstream of the injection zone comprising a zone for disengaging gas, the fluidisation rate by a fluidisation gas being between 0.1 and 30 cm/s, the flow of catalyst flowing by gravity into the injection zone is regulated, the feed is injected into the injection zone below the catalyst shaping member, counter-current to the direction of flow of the catalyst and at an injection angle which is predetermined as a function of the linear momentum of the feed and of the linear momentum of the catalyst, and the mixture containing the vaporised feed is caused to flow in the reaction zone or dropper.

The flow of catalyst which moves by gravity towards the constriction with a variable or constant cross-section of flow is usually between 200 and 20 000 kg/m².s, and preferably between 1 000 and 10 000 kg/m².s, an excellent range of values being between 4 000 and 6 000 kg/m².s.

Advantageously, the feed can be injected by means of a plurality of injectors arranged all around the wall of the injection zone at an angle which is less than or equal to 30 degrees relative to the horizontal, and preferably at an angle of 5 to 25 degrees.

Usually, the injection angle β is determined in such a way that the resultant of the vectors standing for the linear momentum of the feed and the linear momentum of the catalyst is substantially horizontal, e.g. at about 10 degrees to the horizontal. To be more exact, the ratio of the catalyst by weight to the feed in the injection zone can be between 5 and 20, preferably between 10 and 18. The rate of catalyst flowing by gravity through the constriction can be between 0.1 and 20 m/s, and advantageously between 0.5 and 5 m/s, whereas the rate of the atomised feed droplets is usually between 50 and 100 m/s, and preferably between 70 and 90 m/s.

A curtain of catalyst can be formed in two ways:

- in accordance with a first variant, a shaping member can be used for said curtain, comprising a fixed portion attached to the wall of the injection zone and integral therewith and a central movable portion which co-operates with the fixed portion so as to create said constriction with a variable cross-section of catalyst flow. The flow of catalyst in the injection zone for a given flow rate can therefore be controlled by varying the cross-section of flow between said fixed portion and said movable portion of said catalyst shaping member. This method of adjustment is particularly advantageous during start-up of the unit, which is an unsteady state.

- in accordance with a second variant, the curtain of catalyst can be formed by a shaping member which comprises a fixed central portion which co-operates with the wall of the injection zone or with a fixed portion attached to said wall.

The central, fixed or movable, portion according to the variant is advantageously conical or frustoconical in shape, and, together with the wall which is usually cylindrical, defines a constriction with a constant or variable cross-section of flow for the catalyst, depending on the case, and preferably annular. Of course, the central portion which is fixed or movable could be cylindrical, spherical or ovoid in shape. Members of this kind for shaping the catalyst are described in the Applicant's Patent (FR 2631857) which is incorporated herein by reference and which also teaches about injecting a feed perpendicularly to the direction of flow of the catalyst.

- in accordance with a third variant, the catalyst can pass through a constriction in said shaping member which has a substantially constant but circular cross-section of flow.

It is possible to adjust the flow rate of catalyst in the injection zone using a valve with variable opening which can be that in accordance with the first variant, or a valve with variable opening which is placed in the line for introducing hot regenerated catalyst from the regenerator to the conditioning zone. This valve is also controlled by a temperature sensor at the dropper outlet.

According to one feature of the process, the catalyst conditioning zone can comprise a zone for disengaging gas from the catalyst above the dense fluidised bed at a level which is between one third and one half of the total height of the conditioning zone. It is possible to equalise the pressures in the conditioning zone and in the regeneration zone using a pressure equalisation line which connects the disengaging zone to the upper part of the regeneration zone. Under these conditions, the heights of the dense fluidised beds in the conditioning zone and in the regeneration zone are substantially the same.

Since gas can easily be disengaged from the catalyst in a sufficiently large volume in the disengaging zone, there are substantially no bubbles of fluidisation gas rising up in the catalyst supply line coming from the regenerator, and therefore the course of solids is not disturbed.

The size of the injection chamber of the reaction zone is usually such as to enable it to receive a given mass of catalyst, so that the residence time in that zone is usually between 0.02 s and 0.5 s, and preferably between 0.03 s and 0.1 s.

The catalyst can be one of those known to the skilled person, e.g. those cited in US Patent 5296131.

The means for introducing the hydrocarbon feed can be any means known to the skilled person which permits the introduction of a hydrocarbon feed, preferably in the form of droplets which preferably have a mean diameter of less than 5×10^{-4} metres (m), and advantageously of less than 1×10^{-4} (m). It is preferable if the hydrocarbon feed is introduced in such a way that fine droplets are formed which are distributed homogeneously in the introduction zone. An auxiliary fluid, called atomising fluid, which promotes the production of fine droplets can also be introduced with the hydrocarbon feed. This auxiliary fluid is usually a gas such as steam, or a gas which is relatively rich in hydrogen or in hydrogenated compounds coming from other units in the refinery.

Atomisation usually takes place outside the reaction zone.

Usually, the ends of conventional type injectors open into the inside of the injection zone. The jet of droplets of feed which is substantially equal in size to that of the particles and which is at an injection angle according to the invention breaks the falling curtain, or falling stream, of catalyst.

These injectors are usually placed at the periphery of the injection zone, under the catalyst shaping member, and their ends are located in at least one plane which is substantially perpendicular to the axis of the injection zone or of the dropper.

The distance of these injectors, starting from the theoretical points of impact of the jets of feed on the axis of the injection zone (or of the reaction zone), to the lowest point of the catalyst shaping member is at the most equal to twice the diameter of the injection zone.

Preferably, this distance can be between 0.5 and 1 times the diameter of the injection zone.

By optimising this distance and the injection angle of the counter-current feed as well as the flow of catalyst flowing through the constriction, it is possible to significantly improve gasoline selectivity.

The invention is also concerned with a catalytic cracking unit comprising a dropper reactor for catalytically cracking a hydrocarbon feed in the presence of a cracking catalyst and for producing an effluent of light products and of coked cracking catalyst. The unit comprises a member having a constriction for shaping catalyst upstream of the dropper, a feed supply which communicates with an injection chamber at the upper portion of the dropper and which contacts the feed with the shaped catalyst, a vessel for separating the effluents from the coked catalyst in the lower portion of the dropper, and at least one chamber for regenerating coked catalyst and communicating with the separation vessel, and a line for supplying regenerated catalyst which

connects the regeneration vessel to the catalyst shaping member, said unit being characterised in that it comprises a vessel for conditioning the regenerated catalyst into a dense fluidised bed connected between the regenerator and the catalyst shaping member, said vessel comprising fluidisation means and having a zone for disengaging catalyst from gas, of suitable volume, in the upper portion of said vessel, which communicates with the upper portion of the regeneration vessel via a line for equalising pressures, and in that the feed injection chamber comprises a plurality of injectors connected to the feed supply line and which introduce the feed counter-current to the flow of catalyst, below the catalyst shaping member, towards the axis of said chamber at an angle which is less than or equal to 30 degrees relative to the horizontal.

The injection will be better understood in the light of the drawing which illustrates the process and apparatus along a longitudinal axis.

According to Figure 1, a per se known entrained fluidised bed catalytic cracking apparatus 1 essentially comprises a dropper (descending reactor) 13, the upper portion of which is supplied with catalyst which has been conditioned in a conditioning chamber 2. That chamber is supplied with catalyst via an inclined line 3 originating from a regeneration zone containing in this particular case two fluidised bed regenerators 4 and 17 in superposed relationship.

The upper portion of the dropper is supplied with a feed which is introduced by injectors 12 and which is vaporised in contact with the hot regenerated catalyst (approx. 780°C). The effluents are separated from the catalyst in a per se known stripper 14, are removed via a line 15, whilst the catalyst, once stripped using steam, for example, and containing coke, is recycled to the first regenerator 17 by a recycle line 16. The partially regenerated catalyst, in the presence of a gas containing oxygen, rises up into the second regenerator 4 by means of a lift 25 where it undergoes a second combustion step in the presence of a gas containing oxygen. The presence of cyclones or fluidisation means in the separator or regenerators which are well-known

to the skilled person will not be discussed here, and, for the sake of simplicity, they are not shown in the drawings.

To be more exact, the hot regenerated catalyst coming from the second dense fluidised phase regeneration zone is introduced by gravity through inclined line 3 into the conditioning chamber 2 as a dense fluidised phase upstream of the dropper 13.

A fluidisation ring 5 supplies a fluidisation gas 5a which can be steam to the lower portion of the catalyst conditioning chamber at a rate of 10 cm/s. The density of the catalyst is therefore between 550 and 800 kg/m³, for example, and typically, 600 kg/m³.

The size of the catalyst conditioning chamber 2 is such that in its upper portion it has a zone 8 for disengaging gas from the catalyst, located above the inlet to line 3, and at a height which is between one third and a quarter of the total height of the conditioning chamber. A pressure equalising line 9 connects the disengagement zone to the upper portion of the second regenerator.

Under these conditions, the level 7 of the fluidised bed in the second regenerator controlled by a level gauge 23 and controlled by an air flow regulator 24 for lifting the catalyst, corresponds substantially to that at 6 for the fluidised bed in the conditioning vessel.

Downstream of the conditioning vessel 2, the apparatus comprises an injection chamber 10 whose diameter is at least equal to that of the dropper, at the inlet to which a flow regulation valve, or valve for shaping a falling curtain of catalyst, allows a flow of catalyst of approx. 800 kg/m².s through its annular opening or constriction.

This valve can have a central fixed portion, or insert, which, together with the wall of the injection zone, determines the cross-section of flow of the catalyst which is determined in combination with another flow rate regulation valve 19 in the catalyst admission line 3.

According to another variant, not shown, the curtain shaping valve can comprise a central movable portion which is connected to a rod, according to FR Patent 2631857, this rod being protected from the catalyst by a sleeve containing a flushing gas. Said central movable portion of the valve and its seat determine an annular cross section of flow which is suitable for a given flow rate of catalyst supplied by the regulating valve 19 and thus determines a suitable flow.

The diameter of the injection chamber is usually greater than that of the constriction (the maximum diameter of the annular curtain of catalyst formed), so that the ends of the feed injectors do not intercept the curtain of catalyst.

After having been atomised outside the apparatus, the feed is injected through a plurality of injectors 12 placed at the periphery, in a plane which is substantially perpendicular to the axis of the dropper, and the jet of droplets of feed of which is directed towards said axis at an angle of inclination of close to 25 degrees beneath valve 11, counter-current to the falling curtain of catalyst, so that it breaks it up.

The distance of the injectors, starting from the theoretical points of impact of the jets of feed on the axis of the injection chamber (or dropper), to the lowest point of the catalyst curtain shaping member is at the most equal to twice the diameter of the injection chamber, and is preferably between 0.5 and 1 times that diameter.

This distance of the injectors from the valve 11 prevents erosion of the valve, on the one hand, and avoids re-circulation zones above the injectors of the catalyst and/or the feed, on the other hand.

The feed is in this way vaporised in contact with the hot catalyst, and the mixture can then flow towards the bottom of the dropper 13 where the cracking reaction takes place. The diameter of this dropper can be less than that of the injection chamber.

The cracking effluents are recovered via line 15 after steam stripping, and the catalyst is recycled to the first regenerator 17.

The flow rate regulating valve 19 is usually controlled by a line 22 to a temperature measurement 20 indicated by a sensor 21 in the lower end of the dropper.

The unit is generally started up by closing the variable flux constriction 11, or by closing an on-off valve which is not shown in the drawings and which may be placed under the member 11, for example, when this latter has a fixed central portion and determines a constant cross-section of flow for the catalyst.

These operations enable the catalyst conditioning vessel to be filled to a suitable level by virtue of the flow rate valve 19 and the pressure equalisation line 9.

The portion of the catalyst shaping member facing the injected feed can be concave in form, and, in this way, can define a confinement zone for vaporisation of the feed and improve the selectivity of the cracking reaction.

Example

A petroleum feed with a density of $d_4^{15} = 0.95$ and a 50% distillation temperature $T_{50} = 510^\circ\text{C}$ is introduced into a dropper catalytic cracker under the following operating conditions according to the invention:

Catalyst: type Octa 4 from Grace Davidson

Grain density: 1280 kg/m^3

Mean diameter: 75 micrometres

Flow rate of catalyst: 1 t/h

Catalyst/feed (c/o) weight ratio: = 17

Fluidisation rate in the conditioning zone: 15 cm/s corresponding to a density of 580 kg/m^3 .

Flow of catalyst through the annular cross-section of flow: $980 \text{ kg/m}^2 \cdot \text{s}$

Speed of droplets of atomised feed: 70 m/s

Temperature at outlet from the second regenerator equal to temperature of the catalyst conditioning zone: 780°C

Temperature at dropper outlet: 550°C.

The distance along the axis of the feed injectors with respect to the insert (lowest point) is 0.5 times the diameter of the injection chamber.

The following comparative table shows the influence of the injection angle of the feed, the other operating parameters remaining constant:

Yield in weight %	Co-current injection $\beta = -10$ degrees	Counter-current injection		Crossed current injection $\beta = 0$ degrees
		$\beta = 35$ degrees	$\beta = 22$ degrees	
LPG + dry gases	22.5	26	24	23
C5 gasoline $\rightarrow 210^\circ\text{C}$	39.0	41	41	40
LCO $210^\circ\text{C} - 380^\circ\text{C}$	18.5	17	17.6	18.5
Slurry 380°C^+	12.0	8	9.6	11
Coke	8	8	7.8	7.5

The example shows the advantage of injecting the feed counter-current to the catalyst ($\beta = 22$ degrees) in comparison with co-current injection or counter-current injection but at an angle of more than 30 degrees, combined with the introduction into the injection chamber of a catalyst, in the form of a curtain, of suitable density and throughput.

In this way, conversion of heavy products is promoted, which is to the advantage of light feeds which are more readily upgraded (gasoline and LPG) due to better contact of the hot catalyst and droplets of feed.

**CLAIMS**

1. A process for the fluidised bed catalytic cracking of a petroleum feed into lighter effluents in a catalytic cracking zone comprising a reaction zone (13), or dropper, into an upper end of which, termed the injection zone (10), regenerated catalyst coming from at least one regeneration zone (4) is introduced, the catalyst is shaped by means of a shaping member (11) having a constriction, the catalyst is contacted with the feed, a downward flowing mixture of catalyst and feed is formed, at least the majority of the feed is vaporised in said injection zone, said feed is cracked in order to obtain lighter effluents, the effluents are separated from the spent catalyst in a separation zone (14) at the lower end, the effluents are recovered, and the spent catalyst is recycled to the regeneration zone, the process being characterised in that the regenerated catalyst coming from the regeneration zone (4) is caused to flow into a zone (2) for conditioning the dense fluidised bed catalyst upstream of the injection zone comprising a zone (8) for disengaging gas, the fluidisation rate by a fluidisation gas being between 0.1 and 30 cm/s, the flow of catalyst flowing by gravity into the injection zone is regulated, the feed is injected into the injection zone below the catalyst shaping member, counter-current to the direction of flow of the catalyst and at an injection angle which is predetermined as a function of the linear momentum of the feed and of the linear momentum of the catalyst, and the mixture containing the vaporised feed is caused to flow in the reaction zone.

2. A process according to claim 1, wherein the catalyst/feed (c/o) weight ratio in the injection zone is between 5 and 20, and preferably between 10 and 18.

3. A process according to claim 1 or claim 2, wherein the rate of the catalyst in the injection zone is between 0.1 and 20 m/s, and preferably 0.5 to 5 m/s, and the rate of the atomised feed is between 50 and 100 m/s, and preferably between 70 and 90 m/s.



4. A process according to one of claims 1 to 3, wherein a curtain of catalyst is formed by means of the catalyst shaping member which comprises a fixed portion which is integral with the wall of the injection zone and a central movable portion which co-operates with said fixed portion in order to create said constriction with a variable cross-section of flow.
5. A process according to one of claims 1 to 4, wherein the flow of catalyst is regulated for a given flow rate in the injection zone by varying the cross-section of flow between the fixed portion and the movable portion of said catalyst shaping member.
6. A process according to one of claims 1 to 3, wherein the catalyst is caused to flow by gravity through the catalyst shaping member which comprises said constriction with a constant cross-section of flow.
7. A process according to one of claims 1 to 6, wherein a flow of catalyst of between 200 and 20 000 kg/m².s, and preferably of between 1 000 and 10 000 kg/m².s, is caused to flow through the flow cross-section.
8. A process according to one of claims 1 to 7, wherein the residence time in the feed injection zone is between 0.02 s and 0.5 s.
9. A process according to one of claims 1 to 8, wherein the catalyst conditioning zone comprises the zone (8) for disengaging gas above the fluidised bed at a level which is established at substantially that of the fluidised bed in the regeneration zone and at a height between one quarter and one half of the total height of the catalyst conditioning zone, and in which the pressures in the conditioning zone and in the regeneration zone are equalised by means of an equalisation line (9) which connects the disengaging zone to the upper part of the regeneration zone.



10. A process according to one of claims 1 to 9, wherein the angle at which the feed is injected is less than or equal to 30 degrees, excluding zero degrees, and is preferably between 5 and 25 degrees.
11. A process according to one of claims 1 to 10, wherein the diameter of the injection zone is greater than or equal to that of the reaction zone.
12. A process according to one of claims 1 to 11, wherein the distance of the feed injectors from the theoretical points of impact of the jets of feed on the axis of the injection zone (or of the reaction zone) to the lowest point of the catalyst shaping member is at the most equal to twice the diameter of the injection zone.
13. A catalytic cracking unit comprising a dropper (13) for catalytically cracking a hydrocarbon feed in the presence of a cracking catalyst and for producing an effluent of light products and of coked cracking catalyst, a member (11) having a constriction for shaping catalyst upstream of the dropper, a feed supply communicating with an injection chamber (10) at the upper portion of the dropper and for contacting the feed with the shaped catalyst, a vessel (14) for separating the effluents from the coked catalyst in the lower portion of the dropper, and at least one vessel (4) for regenerating coked catalyst and communicating with the separation vessel, and a line (3) for supplying regenerated catalyst which connects the regeneration vessel to the catalyst shaping member, said unit being characterised in that it comprises a vessel (2) for conditioning the regenerated catalyst into a dense fluidised bed connected between the regenerator and the catalyst shaping member, said vessel comprising fluidisation means (5) and having a zone (8) for disengaging catalyst from gas, of suitable volume, in the upper portion of said vessel, which communicates with the upper portion of the regeneration vessel via a line (9) for equalising pressures, and in that the feed injection chamber (10) comprises a plurality of injectors (12) which introduce the feed counter-current to the flow of catalyst, below the catalyst shaping member, towards the axis of said chamber at an angle which is less than or equal to 30 degrees relative to the horizontal.



14. A unit according to claim 13, wherein the catalyst shaping member comprises a fixed portion which is integral with the wall of the injection zone and a central movable portion which co-operates with said fixed portion so as to create said constriction and form a curtain of catalyst.
15. A unit according to claim 13, wherein said catalyst shaping member comprises a constriction with a constant cross-section of flow.
16. A unit according to one of claims 13 to 15, wherein the distance of the feed injectors from the theoretical points of impact of the jets of feed on the axis of the injection zone (or of the reaction zone), to the lowest point of the catalyst shaping member, is at the most equal to twice the diameter of the injection zone.

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