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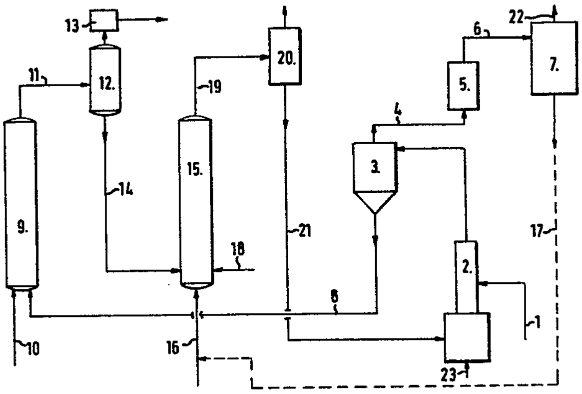
㊹ **Process for the production of light hydrocarbons and synthesis gas.**

㊼ A process for the production of light hydrocarbons (22) and synthesis gas (19), wherein a hydrocarbon-containing feedstock (1) is contacted in a pyrolysis zone (2) with a fluidized particulate heat carrier (21) which is at a sufficiently high temperature to supply the heat required for pyrolysis. A stream containing volatile light hydrocarbons (4) is produced and coke is deposited on the heat carrier. The coke and heat carrier (8) are passed to a combustion zone (9) where the coke is combusted and the heat carrier is heated. The heated carrier (14) is passed to a gasification zone (15) where the heat in the carrier is used to gasify a carbonaceous feedstock (16). The heat carrier which is then at the temperature required for pyrolysis is subsequently passed (21) to the pyrolysis zone (2) to complete the cycle.



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PROCESS FOR THE PRODUCTION OF LIGHT HYDROCARBONS AND SYNTHESIS GAS

This invention relates to a process for the production of light hydrocarbons and synthesis gas.

Rapid escalation of chemical feedstock costs in recent years has spurred efforts to utilize sources which were previously considered uneconomic. One result of such efforts is the development of processes for the cracking of heavier crude oil fractions in order to produce ethylene and other chemical feedstocks.

One difficulty inherent in the utilization of such fractions is that they are so hydrogen-deficient that the yield of valued materials is lower and the capital and operating costs are increased. On the other hand, in general, heavier and higher sulphur feedstocks have a decreasing range of end uses and are valued accordingly. Thus, such feedstocks appear to be economically attractive. One process, that described in U.S. patent specification 2,527,575, utilizes heavy feedstocks in a multi-stage process, the method being characterized by severe heat treatment to coke the feedstock and produce, inter alia, some normally gaseous hydrocarbons. However, the apparent severity of the coking procedure described would limit the volume of gaseous hydrocarbons produced. Accordingly, a cracking process which capitalized on the relatively low cost of heavy feedstock materials, overcame the environmental and disposal problems associated with the residual products, and which produced good yields of light olefins and other useful products could have great economic importance. The present invention provides such a process.

Accordingly, the invention provides a process for the production of light hydrocarbons and synthesis gas, comprising:

(a) continuously feeding a hydrocarbon-containing feedstock and a particulate heat carrier to a pyrolysis zone, the particulate heat carrier being preheated sufficiently to supply the heat required for pyrolysis and being fluidized or entrained in the pyrolysis zone by an inert fluidizing or entraining gas, contacting the feedstock and the heat carrier in the pyrolysis zone to produce a product stream containing light hydrocarbons and heavy residual products, and a cooler particulate heat carrier having carbonaceous deposits thereon, continuously separating the product stream from the particulate heat carrier, and recovering the light hydrocarbons in the product stream;

(b) continuously separating cooler particulate heat carrier having carbonaceous deposits thereon from the pyrolysis zone and passing said cooler particulate heat carrier to a heat exchange zone where the carbonaceous deposits are combusted with an oxygen-containing gas to heat the heat carrier sufficiently to supply the heat required for the synthesis gas generation of step (d);

(c) continuously removing the particulate heat carrier from combustion gases and passing said heat carrier to a synthesis gas generation zone;

(d) continuously feeding a carbonaceous feedstock and the particulate heat carrier to the synthesis gas generation zone, the particulate heat carrier being fluidized in said synthesis gas generation zone, contacting the carbonaceous feedstock with steam and said fluidized heat carrier in said synthesis gas generation zone to produce synthesis gas and a particulate heat carrier at the temperature required for pyrolysis in step (a), and recovering the synthesis gas; and

(e) continuously separating the particulate heat carrier from the synthesis gas generation zone and passing said particulate heat carrier to the pyrolysis zone of step (a) to provide the particulate heat carrier of step (a).

Preferably, the heat carrier in step (a) is at a temperature of 815-1093°C and in step (b) the heat carrier is heated to a temperature of 927-1260°C.

The product stream from the pyrolysis zone may be quenched, and conventional separation, including fractionation, procedures may be employed to separate and recover the light hydrocarbon materials. In a preferred embodiment of the invention, the bottoms fraction from the separation zone is used as the feed to the synthesis gas generation zone. The invention thus provides a process for the production of olefins which allows advantageous disposition of low value coke and heavy oil by-products without production of troublesome gas with a low calorific value.

The composition of the hydrocarbon-containing material employed as the feed to the pyrolysis zone is widely variable. Any suitable hydrocarbon-containing feedstock may be employed, but the real value of the invention lies in the ability to treat heavy oils including residual oils, such as topped or reduced crude mineral oils. Crude oil, synthetic crude oil, long residues, shale oil, coal oils, and mixtures thereof, may be used. "Pitch", a product that even to-day poses disposal problems, is eminently suitable. Higher grade materials, such as gas oils, may also be used. In sum, any material which contains sufficient hydrocarbonaceous material which may be cracked to produce the products desired, is suitable.

The pyrolysis zone will be operated under conditions to crack the hydrocarbonaceous material to produce light hydrocarbons, such as ethylene and propylene. Because conditions vary from feedstock to feedstock, conditions of pressure, temperature, space velocity, etc., are widely variable.

In general, appropriate temperatures in the pyrolysis zone will range from 693-927°C, with temperatures of from 732-871°C being preferred. As indicated, the heat will be supplied primarily by finely divided fluidized heat carrier particles, the particles being supplied preferably at a temperature of 815-1093°C or more, preferably 871-982°C. Pressures are not critical, and may be suitably adjusted by those skilled in the art. Generally, pressures less than 5 atmospheres are preferred.

The composition of the finely divided solid heat carrier may be varied widely. Suitable inert solid heat carrier materials are well known in the art, and the particular heat carrier chosen is a matter of choice, given the requirements outlined herein. The heat carrier may also contain suitable catalytic agents to assist in the reaction, but this is not a requirement of the invention. Average particle size will usually range from 50 microns to 1000 microns, with average particle sizes of 50 microns to 300 microns being preferred. Preferred heat carrier materials include alumina and coke. Coke is particularly advantageous since in that case no extraneous materials are present in the system.

The particles and the feedstock may be fluidized or entrained with a suitable gas which is at least substantially inert to the feedstock, carrier or products. Steam, inert gases, water gas, natural gas, flue gases or the like may be used to fluidize the solids. If desired, a portion of the heat required in the pyrolysis zone may be supplied by partial combustion within the zone. An oxidizing gas, such as air or oxygen or mixtures thereof, may replace part of the fluidizing gas for this purpose. Generally, the carrier will be entrained or fluidized in a high velocity gas stream, contacted with the atomized or vaporized feedstock, and quickly separated. Sufficient fluidizing gas is used, e.g., 0.3-3.0 kg per kg of feedstock, to entrain or fluidize the heat carrier and reduce the partial pressure of the pyrolysis products.

Control of the feed rate of the feedstock, fluidizing gas and heat carrier will be varied, depending on the feedstock, to provide, under the heat transfer conditions in the entrained flow or fluidized bed, a relatively short residence or contact time of the pyrolysis products. This contact time is critical, in order, under the conditions mentioned, to preserve high yields of the relatively reactive olefinic products. While the residence time will vary, the total residence time of the feed and products in the pyrolysis zone will generally be from 0.09 second to 3 seconds, preferably from 0.3 second to 1.0 second. After suitable contact of the heat carrier and the feedstock, the carrier must be separated from the products formed. Separation is readily accomplished by appropriate inertial devices, such as a cyclone. The particular means or devices chosen for separation of the heat carrier from the product stream are well known to those skilled in the art.

As indicated, the products from the pyrolysis or cracking zone are treated for recovery of the desired light hydrocarbons. Generally, after separation from the heat carrier, the product stream will be quenched and sent to appropriate separation equipment. Normally, the quench will lower the temperature of the product stream to 315-649°C, either in one or more stages. In the separation of the desired fractions of the product stream, a bottoms fraction will be produced which is undesired as a conventional feedstock, but which has useful carbon values. In a preferred embodiment of the invention, this bottoms fraction is used as the feed to the synthesis gas generation zone.

Spent heat carrier material, i.e., that which has transferred a substantial portion of its heat in the pyrolysis zone, is passed, after separation from the product stream, to a combustion zone where the coke deposited during pyrolysis is burned. In the continuous process of the invention, the combustion zone suitably comprises a lift pipe heater or a dense phase fluidized bed, and variables such as gas velocity, reactor size, etc., may be adjusted by those skilled in the art. An oxygen-containing gas, preferably air, is supplied to the combustion zone in sufficient quantity to provide sufficient oxygen to complete combustion of the coke deposited on the carrier and any supplemental fuel, if supplied, to heat the carrier to the required temperature which is suitably in the range of 927-1260°C. In general, the oxygen-containing gas will be supplied in an amount equivalent to 100 per cent to about 150 per cent of the stoichiometric requirement. If coke is used as the carrier material, the amount of oxygen supplied is regulated more carefully. Excess oxygen, in the case of coke as a heat carrier material, will preferably be limited to not more than about 10 per cent excess. The off-gas from the combustion zone may be treated in known fashion.

After separation from the off-gas, the hot heat carrier is passed to a synthesis gas generation zone where, in fluidized form, it contacts an atomized heavy residue material and hot steam to produce synthesis gas. As indicated, the temperature of the heat carrier entering the synthesis gas generation zone will preferably be from 927-1260°C. The heat expended in generating the synthesis gas will lower the temperature of the heat carrier by about 37-113°C. Oxygen may also be supplied to the synthesis gas generation zone to increase conversion of the residue and to provide some of the heat requirement through partial combustion. Nonetheless, the bulk of the heat required is supplied by the heat carrier material. The carrier is fluidized by any suitable gas, preferably superheated steam, carbon dioxide or mixtures thereof.

Either a dense phase or fast fluidized bed gasifier may be used, with a fast fluidized bed preferred. It is an advantage of the invention that a variety of carbonaceous feedstocks, such as heavy carbonaceous feeds or residues may be used for this zone, but the most convenient feed, which may or may not be supplemented, is the bottoms fraction from the pyrolysis product stream recovery system. Other carbonaceous feedstocks, such as pitch, coal tars, coal, etc., may be used. The heat carrier, having spent only a minor portion of its heat, is then sent to the pyrolysis zone, thus closing the loop and recommencing the cycle.

The invention is further illustrated with reference to the accompanying drawing.

A vacuum pitch in line 1 is atomized into a steam (supplied through line 23) fluidized riser column (2) where it contacts a hot heat carrier (e.g., 1037°C alumina sand). The mixture flows through column (2) into unit (3) where the heat carrier, with deposited coke, and now at a temperature of 760-816°C, is disengaged from the product gases. Residence time is about 0.5 second.

The resulting product gas passes through line 4 to quench zone (5) where the reaction is quenched and the temperature lowered to less than 538°C. Any suitable quench procedure may be utilized. From quench zone (5) the product gas passes through line (6) to separation zone (7) where the product gas is separated into the desired components. Light products leave the separation zone (7) through line (22). Ethylene, propylene, butadiene, gasoline, and other products are recovered, and off-gases may be treated as necessary. As indicated, however, the bottoms from this separation system, containing heavier carbonaceous components, are particularly useful, as will be described more fully hereinafter.

Concomitantly, the heat carrier, after disengagement from the product gas, and with coke deposited thereon, passes through line (8) to combustor (9) where the coke is burned off. Combustor (9) is preferably a line heater or lift pipe combustor, with air being introduced in line (10) in 15 per cent excess (calculated). Supplemental fuel may be added (not shown).

Combustion gas and heat carrier pass through line (11) to a separator, preferably an inertial device (12) where the combustion gas is separated from the heat carrier. The combustion gas may be purified and subjected to heat recovery before exhaust in conventional fashion at (13).

The heat carrier, now at a temperature of about 1204°C, is passed through line (14) to synthesis gas generator (15). In gasifier (15) the heat carrier is contacted as a fast fluidized bed with a heavy residual material supplied by line (16). As noted previously, the preferred feed to this unit is the bottoms from the separation zone (7), the bottoms being supplied via line (17) (dotted line). Steam, in excess, is supplied through line (18), and optionally, a small amount of oxygen, e.g., 20 per cent on a stoichiometric basis. The heavy residue is converted primarily to a stream containing H_2, CO, H_2S and CO_2, and some coke will be left on the heat carrier. By supplying most of the heat to the gasifier with the solid heat carrier instead of by internal partial combustion, the oxygen consumption and unwanted CO_2 production are greatly reduced and the H_2/CO ratio is greatly increased. The heat carrier and product stream leave unit (15) through line (19) and pass to separation zone, preferably an inertial device (20) where the product gas stream and heat carrier are separated. The product gas stream may be processed by conventional technology to produce a chemical grade synthesis gas. Heat carrier, now at a temperature of 1038°C, passes through line (21) to pyrolysis unit (2), recommencing the cycle.

In order to demonstrate the yields and product distribution obtainable by pyrolyzing a pitch feedstock utilizing a high temperature, short residence time procedure, the following experiment was run.

Light Arabian vacuum pitch (58.4 grams) was mixed with coal char prepared from Western sub-bituminous coal, the pitch being added in an amount of about 30 per cent by weight, based on the weight of the char. The mixture was fed into a tubular pyrolysis reactor, under the following conditions:

Temperature	871°C
Pressure	1.09 atm.
Residence time	0.092 seconds
Steam to solids ratio (wt.)	2.591

The yield of products, on a per cent by weight basis, based on the weight of the pitch charged, is as follows:

Hydrocarbon gases	38.9
Methane	5.34
Ethylene	16.37
Propylene	7.48
Light hydrocarbons (32-127°C)	3.7
Heavy hydrocarbons (149°C+)	33.6
Coke	17.8

Broken down more carefully, on a weight basis, the products were as follows:

C_1-C_4	g	%w
Ethylene	9.5034	16.37
Propylene	4.3405	7.48
Methane	3.1002	5.34
Acetylene	0.6527	1.12
Ethane	0.6374	1.10
Methyl acetylene	0.6142	1.06
Butadiene	1.9145	3.30
C_4H_5	1.2848	2.21
C_4H_{10}	0.5000	0.86
	22.5477	38.84
C_5-127°C		
Gasoline	2.1675	3.73
Benzene	0.2867	0.49
Toluene	0.3765	0.65
149°C + heavy oil (5.67%w S)	19.4800	33.56
Coke - (on CHAR)	10.3150	17.77

CLAIMS

1. A process for the production of light hydrocarbons and synthesis gas comprising:

(a) continuously feeding a hydrocarbon-containing feedstock and a particulate heat carrier to a pyrolysis zone, the particulate heat carrier being preheated sufficiently to supply the heat required for pyrolysis and being fluidized or entrained in the pyrolysis zone by an inert fluidizing or entraining gas, contacting the feedstock and the heat carrier in the pyrolysis zone to produce a product stream containing light hydrocarbons and heavy residual products, and a cooler particulate heat carrier having carbonaceous deposits thereon, continuously separating the product stream from the particulate heat carrier, and recovering the light hydrocarbons in the product stream;

(b) continuously separating cooler particulate heat carrier having carbonaceous deposits thereon from the pyrolysis zone and passing said cooler particulate heat carrier to a heat exchange zone where the carbonaceous deposits are combusted with an oxygen-containing gas to heat the heat carrier sufficiently to supply the heat required for the synthesis gas generation of step (d);

(c) continuously removing the particulate heat carrier from combustion gases and passing said heat carrier to a synthesis gas generation zone;

(d) continuously feeding a carbonaceous feedstock and the particulate heat carrier to the synthesis gas generation zone, the particulate heat carrier being fluidized in said synthesis gas generation zone, contacting the carbonaceous feedstock with steam and said fluidized heat carrier in said synthesis gas generation zone to produce synthesis gas and a particulate heat carrier at the temperature required for pyrolysis in step (a), and recovering the synthesis gas; and

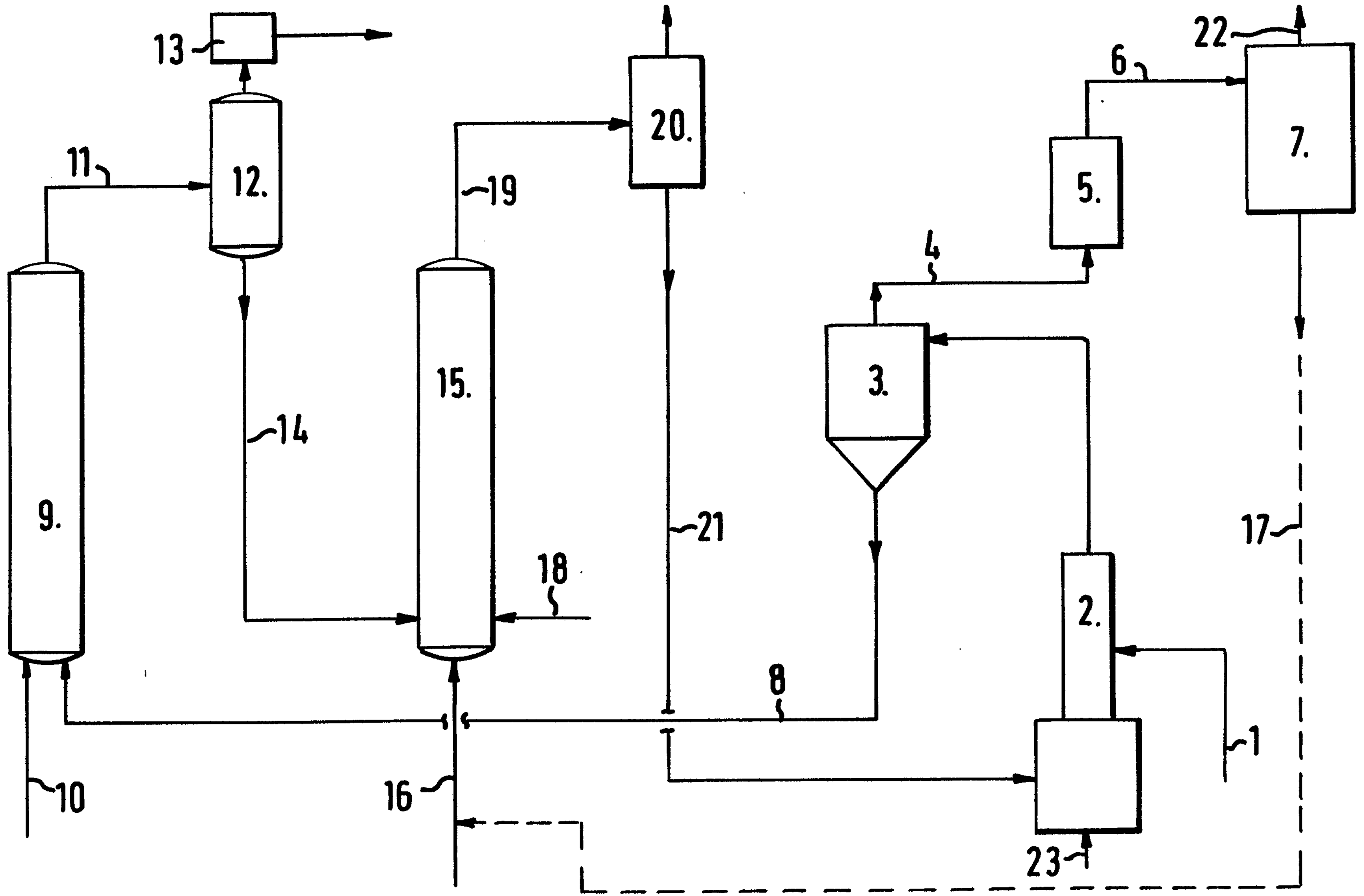
(e) continuously separating the particulate heat carrier from the synthesis gas generation zone and passing said particulate heat carrier to the pyrolysis zone of step (a) to provide the particulate heat carrier of step (a).

2. A process as claimed in claim 1, wherein in step (a) the heat carrier is at a temperature of 815-1093°C and in step (b) the heat carrier is heated to a temperature of 927-1260°C.

3. A process as claimed in claim 1 or 2, wherein the product stream produced in step (a) is quenched and fractionated to produce a heavy carbonaceous residue.

4. A process as claimed in claim 3, wherein the heavy carbonaceous residue is fed continuously as feedstock to the synthesis gas generation zone.

5. A process as claimed in any one of claims 1-4, wherein the total residence time of the feedstock and product stream in the pyrolysis zone in step (a) is from 0.09 to 3.0 seconds.



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European Patent
Office

EUROPEAN SEARCH REPORT

0012468
Application number
EP 79 20 0711

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
A	US - A - 4 062 760 (D.E. BLASER) ----	

CLASSIFICATION OF THE APPLICATION (Int. Cl. ³)

C 10 G 9/32
C 01 B 3/34
C 10 G 51/06

TECHNICAL FIELDS SEARCHED (Int.Cl. ³)

C 10 G 9/32
9/28
51/06
51/00
C 01 B 3/34

CATEGORY OF CITED DOCUMENTS

X: particularly relevant
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: conflicting application
D: document cited in the application
L: citation for other reasons

&: member of the same patent family, corresponding document

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

Place of search	Date of completion of the search	Examiner
The Hague	20-03-1980	LO CONTE

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