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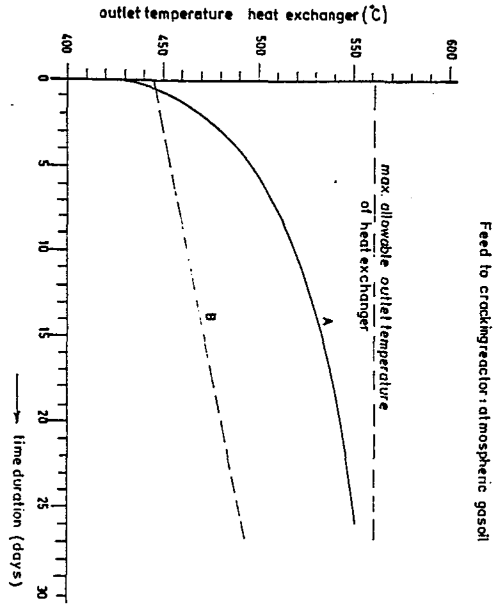
### (54) Installation (plant) for thermo-cracking a hydrocarbon starting material to alkene, shell and tube heat exchanger for use in such an installation and process for manufacturing shell and tube heat exchanger.

(57) The invention relates to an installation (plant) for thermocracking a hydrocarbon starting material to alkenes, comprising a cracking furnace with externally heated reactor tubes (coils) and a shell and tube heat exchanger («quench», cooler, «transfer line» heat exchanger, TLX) to be used for quenching the reactor effluent and connected to the cracking furnace, wherein on the shell side steam is generated, wherein the internal surface of the tubes of the heat exchanger is coated with an inert layer impermeable to the materials in the reactor effluent which are responsible for the fouling, said layer masking the alloy of which the heating exchanger tubes consist. Said layer has a thickness of preferably 0.5 – 20 µm and is a layer based on an inert metal, in particular aluminium, metal oxide, aluminate, silicate or graphite or is an inert polymeric layer, in particular a layer formed by thermosetting alkylene quench oil with a peroxide, like benzoyl peroxide. The invention also relates to the heat exchangers.



**EP 0 110 486 A1**

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# INSTALLATION (PLANT) FOR THERMO-CRACKING A HYDROCARBON STARTING MATERIAL TO ALKENE, SHELL AND TUBE HEAT EXCHANGER FOR USE IN SUCH AN INSTALLATION AND PROCESS FOR MANUFACTURING SHELL AND TUBE HEAT EXCHANGER

The invention relates to a plant for thermo-cracking a hydrocarbon starting material to alkenes, comprising a cracking furnace with externally heated reactor tubes (coils) and a shell and tube heat-exchanger connected to the cracking furnace in order to quench the reactor effluent ("quench", cooler, "transfer line" heat exchanger, TLX) wherein steam is generated on the shell side.

Such installations (plants), which are generally used in the preparation of alkenes like ethene and propene from starting materials which may vary from natural gas to naphthas and gas oil, are described in Kirk-Othmer, Encyclopedia of Chemical Technology, third edition, vol. 9 (1980) pages 400-408, in particular pages 403-408.

In the course of time a number of general conditions were found for the cracking furnaces of those installations, which should be met regardless the hydrocarbon starting material, and even control programs controlled by a "computer" were designed, which as to the power balance guarantee an optimum operation of the cracking furnaces and by which is reached, that the cracker furnaces can be operative for some months together.

The reactor effluent of the cracking furnaces is quenched in the shell and tube heat exchanger from 750-900°C to 350-560°C (Kirk-Othmer l.c., page 407, table 5) to prevent that after leaving the cracker furnace, in said effluent still reactions take place under adiabatic conditions, which would affect adversely the yield of alkenes, and simultaneously steam with a pressure of 105-125 bara (bar absolute) is generated.

However when quenching the reactor effluent the inside surfaces of the heat exchanger tubes are fouled, said fouling leading to a decrease in heat transfer while also the sensible heat of the reactor effluent is ever less used for the generation of the high pressure steam. The effluent coming from the shell and tube heatexchanger has an ever increasing temperature.

Up to now it was assumed that this phenomenon cannot be prevented. Generally the phenomenon was ascribed to condensation of heavy hydrocarbon components from the effluent from the cracking furnace onto the colder heat exchanger surfaces followed by continuing dehydrogenation reactions in the condensate at the temperature prevailing on the wall of the heat exchanger tubes (vide Lohr. B & H Dittmann, OGJ, 1978, May 15).

According to Dutch patent application 70 07556 in a different quenching system, wherein a cracker gas mixture is quenched by introducing said gas mixture via an inlet into a quench liquid which is present in a quenching barrel, the problem of fouling and even clogging of the inlet pipe by deposition of tar and carbonaceous materials on the inside of the inlet pipe is prevented, by insulating the inlet pipe on the outer side, so that the temperature of the inside of the inlet pipe remains relatively high and condensation of tar and carbonaceous materials appears less easy on the inside. The insulating layer has a thickness of some centimeters.

This solution is not possible if a shell and tube heat exchanger is used, as insulation of the tubes of shell and tube heat exchanger nullifies (overrides) the entire cooling of the reactor effluent.

It was now found that the fouling on the inside of the heat exchanger can be decreased and/or inhibited, so that the shell and tube heat exchanger can be in operation for a much longer times, if the internal surfaces of the tubes of the heat exchanger are coated with an inert layer, impermeable to the materials from the reactor effluent, which are responsible for the fouling, said layer masking the alloy of which the heat exchanger tubes consist.

Such a layer should have such a thickness, that it is impermeable to the reactor effluent, but on the other hand it should not be so thick that it impedes the heat transfer.

The minimum thickness should preferably be 0.5 µm. Preferably it has a thickness of not more than 20 µm, for, with greater thicknesses, the effect, the temperature drop on the layer, should be too big.

According to a preferred embodiment of the invention the layer substantially comprises graphite, and/or metal and/or metal oxides, metal salts and/or silicates.

A particularly suitable process which can be used to obtain such a layer is, using a viscous mixture of a powdered graphite, metals, metal oxides, metal salts (particle size generally $< 5$ µm) with a silicone based resin in an aromatic solvent. Said mixture is applied with current spraying methods and is thermoset. Thermosetting takes suitably place at tempetatures between 275°C and 375°C for 1½ - 5 h. Said thermosetting (curing) is necessary to vaporize the solvent, and to have reticulation take place in the resin component, and optionally to have the resin component decomposed, while silicon remains enclosed in the layer. The result is that a quasi-continuous layer is formed, with a small specific area. Such a layer is highly wear-resistant and resistant to high temperatures.

The impermeability of the layer can be increased by repeating the process several times. Beside graphite especially metals from group 3 or 4 of the periodical system and their oxides are considered, e.g. aluminium, titanium, zirconium. Also silicates and aluminates can be used.

Especially graphite and aluminium appear to provide the result aimed at (decrease and/or inhibition of the fouling phenomena), while both are cheap and can be easily applied.

Other processes which can be used to apply a metal layer are current techniques like vaporization under vacuum, (vacuum coating or vacuum metalizing), forming a deposit of metal by decomposition of a vaporous metal compound (gas plating).

According to a second embodiment of the invention the impermeable layer on the internal surface of the heat exchanger tubes consists of an inert polymeric layer.

Preferably this is a polymeric layer, formed by applying a mixture of the oily fraction which is recovered when quenching the effluent from the cracking reactor (ethylene quench oil) and of an initiator forming free radicals, in particular a peroxide, like benzoyl peroxide, cumene hydroperoxide, on the internal surface of the tubes, draining the excess and thermosetting the remaining mixture.

Such a layer has a structure which highly resembles the fouling layer which normally appears, and it is stable at the temperatures prevailing in the heat exchanger, so that it does not influence the phenomena which appear in the heat exchanger. On this layer, once formed, only a small fouling layer appears.

The invention also relates to a shell and tube heatexchanger to be used in an apparatus for cracking a hydrocarbon starting material to alkenes, wherein the internal surfaces of the heat exchanger tubes are coated with an inert layer impermeable to the reactor effluent of a cracking furnace for the preparation of alkenes, said layer masking the alloy of which the heat exchanger tubes consist.

The layer by which the internal surfaces of the heat exchanger tubes are coated should preferably meet the above-mentioned conditions.

The invention also relates to a process for manufacturing a shell and tube heatexchanger to be used in an installation for cracking a hydrocarbon starting material to alkenes and resistant to quenching of the effluent from the cracking reactor of such an installation, wherein a polymeric layer is formed by spraying a mixture of the oily fraction which is recovered when quenching the effluent from the cracking reactor (alkylene quench oil) and of an initiator forming free radicals onto the internal surface of the tube and thermosetting it.

In said process preferably a peroxide is used as catalyst, in particular benzoyl peroxide, as peroxides in the polymerisation of alkenes and alkene mixtures are effective catalysts.

The amount of catalyst may vary within wide ranges but preferably a mixture is used which comprises 0.5 - 3% of catalyst, as with such a mixture quickly a good polymer layer can be obtained.

The effect which is obtained with the installation according to the invention is elucidated in the following examples.

Example I

In a current installation for the preparation of ethene,with a capacity of 40000 tons/year ethene, gas oil was cracked. The effluent of the cracking furnace had the following composition.

| Effluent composition (weight %) | | |
|---|---|---|
| $H_2$ | 0.49 | |
| $CH_4$ | 8.21 | |
| CO | 0.02 | |
| | | 8.72 |
| $C_2H_2$ | 0.16 | |
| $C_2H_4$ | 21.22 | |
| $C_2H_6$ | 2.87 | |
| | | 24.25 |
| methyl-acetylene | 0.16 | |
| prepadiene | 0.12 | |
| $C_3H_6$ | 13.61 | |
| $C_3H_8$ | 0.41 | |
| | | 14.30 |
| $C_4H_6$ | 4.86 | |
| $C_4H_8$ | 6.57 | |
| $C_4H_{10}$ | 0.05 | |
| | | 11.48 |
| $C_5$ until | 6.21 | |
| benzene | 2.82 | |
| $C_6$ (NA) | 2.05 | |
| toluene | 2.22 | |
| $C_7$ (NA) | 0.67 | |
| o-xylene | 0.26 | |
| m-xylene | 0.43 | |
| p-xylene | 0.20 | |
| ethyl benzene | 0.32 | |
| styrene | 0.40 | |
| $C_8$ (NA) | 0.15 | |
| $C_9$ until | 2.68 | |
| $C_{10}$ and higher | 11.83 | |
| | | 41.25 |
| | 100.0 | |

NA = non - aromatic

Said effluent, which had a temperature of 800-850°C and a pressure of 1.6 bara was quenched in two just cleaned shell and tube heat exchangers (TLX) connected in parallel, while on the shell side of the heat exchangers steam with a pressure of 110 bara was generated.

One TLX (A) had heatexchanger tubes made from a nickel-chromium-alloy which is usual for this type of tubes.

The other TLX (B) had heat exchanger tubes from the same nickel chromium alloy, the internal surface of which was coated with a 5 μm thick aluminium based layer applied in 3 steps.

The temperature of the quenched effluent coming from the TLX (A) in the beginning of the test was 420°C and the temperature of the quenched effluent coming from TLX (B) was 450°C.

The variation in the temperature of the effluents coming from both TLX against the time duration of the test is elucidated in the figure.

Curve A shows the result for TLX (A).
Curve B shows the result for TLX (B).

One sees that with TLX (A) (Curve A) the temperature of the effluent coming from the TLX, increased to 500°C in about 5 days and during the rest of the test the temperature gradually further increased, until after 26 days the maximum allowed temperature of 560°C was obtained.

The fouling rate in TLX (B) (Curve B) was substantially constant and the extrapolated attainable hours of service will be 60 days in stead of 26 like for TLX (A).

Herefrom it follows that with the second TLX the heat transfer during the whole test was better than with the first TLX.

Both TLX's were thrown out of operation and were inspected.

TLX (A) appeared to comprise a thick fouling layer.

In TLX (B) only a slight fouling was present.

Coating the internal surface of the heat exchanger tubes of TLX (B) was carried out by spraying a mixture of 12% by weight of aluminium powder with a particle size of < 2 µm, 48% by weight of a silicone resin comprising methyl groups and phenyl groups, and 40% by weight of toluene into the tube, draining the excess and heating the remaining layer for 2 hours at 300°C, thus vaporizing the toluene and reticulating the resin, repeating this processing once, and finally repeating the treatment once with a mixture of 10% by weight of aluminium powder with a particle size of < 2 µm, 40% by weight of the same silicone resin and 50% by weight of toluene.

Example II

The test of example I was repeated, while a TLX (C) was used, the heat exchanger tubes of which were coated on the inside with a 5 µm thick layer based on graphite, which was applied as follows:

A mixture of 24% by weight of graphite having a particle size of < 1 µm, 36% by weight of the same silicone resin as was used when forming the coating according to example I and 40% by weight of toluene was introduced into the tubes, the excess was drained off and the remaining layer was heated for 2 hours at 300°C at which temperature the toluene was vaporized and the resin was subjected to reticulation. This processing was repeated once and finally the processing was repeated once with a mixture of 20% by weight of graphite having a particle size $< 1\ \mu m$, 30% by weight of the same siliconeresin and 50% by weight of toluene.

The variation in the temperature of the effluent coming from said TLX (C) against the time corresponded to the variation in the temperature of the effluent coming from TLX (B) (example I) against the time.

At the end of the test the heat exchanger tubes were inspected; only a slight fouling was observed.

Example III

A similar test was carried out as in example I, wherein now a TLX (D) was used having heat exchanger tubes the internal surface of which was coated with a polymeric layer, formed by mixing the oily fraction obtained when quenching the effluent from the cracking reactor (ethylene quench oil) with 1.5% of benzoyl peroxide and introducing said mixture into the heat exchanger tubes, draining off the excess and externally heating the tubes at 400°C.

The variation in the temperature of the effluent coming from TLX (D) also corresponded to curve B of the figure. At the end of the test the heat exchanger tubes of TLX (D) were inspected. On the polymeric layer a slight fouling had been deposited.

CLAIMS

1. Installation (plant) for thermocracking a hydrocarbon starting material to alkenes, comprising a cracking furnace with externally heated reactor tubes (coils) and a shell and tube heat exchanger ("quench" cooler, "transfer line" heat exchanger, TLX) to be used for quenching the reactor effluent and connected to the cracking furnace, wherein on the shell side steam is generated. characterized in that, the internal surfaces of the tubes of the heat exchanger are coated with an inert layer impermeable to the materials in the reactor effluent which are responsible for the fouling, said layer masking the alloy of which the heating exchanger tubes consist.

2. Installation according to claim 1, characterized in that the inert coating layer impermeable to the materials in the ractor effluent which are responsible for the fouling, has a thickness between 0.5 $\mu m$ and 20 $\mu m$.

3. Installation according to claim 1 or 2, characterized in that the inner surfaces of the tubes of the heat exchanger are coated with a layer based on an inert metal, metal oxide, aluminate and/or silicate.

4. Installation according to claim 3, characterized in that the

layer based on inert metal consists of a coating based on aluminium.

5. Installation according to claim 1 or 2, characterized in that the tubes of the heat exchanger are internally coated with a layer based on graphite.

6. Installation according to claim 1 or 2, characterized in that the tubes of the heat exchanger are internally coated with an inert polymeric layer.

7. Installation according to claim 6, characterized in that the polymeric layer is formed by applying a mixture of the oily fraction which is recovered when quenching the effluent from the cracking reactor (alkylene quench oil) and a free radical forming initiator onto the inner surface of the lines, e.g. by spraying, followed by thermosetting said layer.

8. Installation according to claim 7, characterized in that the polymeric layer is formed by applying a mixture of the oily fraction which is recovered when quenching the effluent from the cracking reactor, and a peroxide as initiator onto the surface followed by thermosetting.

9. Shell and tube heat exchanger to be used in an installation for cracking a hydrocarbon starting material to alkenes, characterized in that the internal surfaces of the heat exchanger tubes are coated with an inert layer, impermeable to the reactor effluent of a cracking furnace for the preparation of alkenes, said layer masking the alloy of which the heat exchanger lines consist.

10. Shell and tube heatexchanger according to claim 9, characterized in that the impermeable coating layer, which is inert for the

reactor effluent on the internal surfaces of the heat exchanger tubes has a thickness between 0.5 um and 30 um.

11. Shell and tube heatexchanger according to claim 9 or 10, characterized in that the internal surfaces of the lines of the heatexchanger are coated with a layer based on an inert metal, oxide, silicate.

12. Shell and tube heatexchanger according to claim 11, characterized in that the layer of inert material consists of a coating based on aluminium.

13. Shell and tube heatexchanger according to claim 9 or 10, characterized in that the tubes of the heatexchanger are internally coated with a layer based on graphite.

14. Shell and tube heatexchanger according to claim 9 or 10, characterized in that the tubes of the heatexchanger are internally coated with an inert polymeric layer.

15. Shell and tube heatexchanger according to claim 14, characterized in that the polymeric layer is formed by spraying a mixture of the oily fraction which is recovered when quenching the effluent from the cracking reactor (alkylene quench oil) and of an initiator forming free radicals, onto the internal surface of the lines followed by thermosetting.

16. Shell and tube heatexchanger according to claim 15, characterized in that the polymeric layer is formed, by applying a mixture of the oily fraction which is recovered when quenching the effluent from the cracking reactor and a peroxide as initiator onto the surface followed by thermosetting.

17. Process for the manufacture of a shell and tube heatexchanger, to be used in an installation for cracking a hydrocarbon starting material to alkenes and intended for quenching the effluent coming from the cracking reactor of such an installation, characterized in that the internal surfaces of the heat exchanger tubes are sprayed with a mixture of an oily fraction obtained when quenching the effluent from a cracking reactor for the preparation of alkenes and of an initiator forming free radicals, draining off the excess of the mixture from the heat exchanger tubes and heating the tubes at a temperature at which the mixture is cured.

18. Process according to claim 17, characterized in that as initiator a peroxide is used.

19. Process according to claim 18, characterized in that benzoyl peroxide is used as initiator.

20. Process according to claim 17-19, characterized in that a mixture is used which comprises 1-5% initiator.

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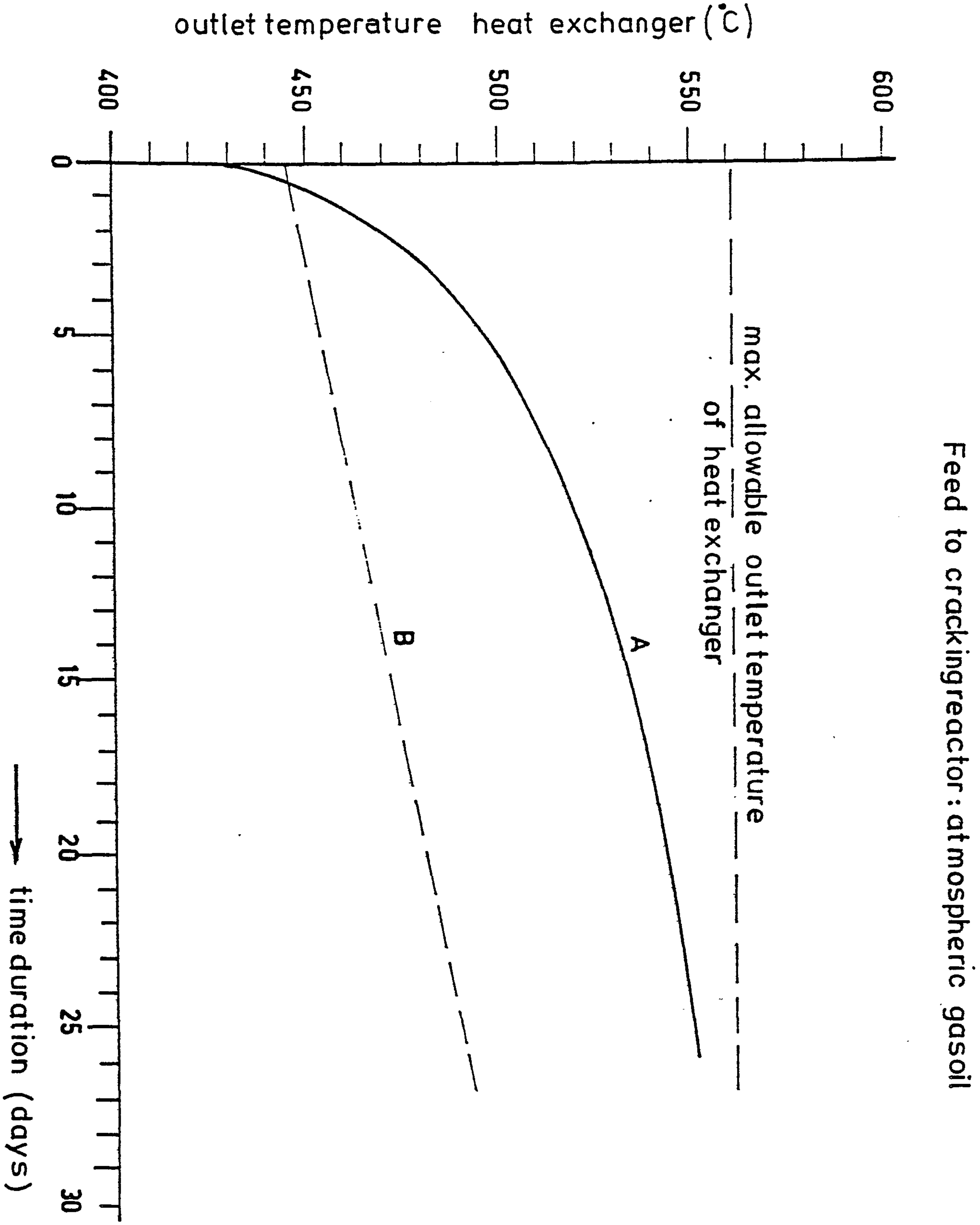
outlet temperature heat exchanger (°C)
400
450
500
550
600
0
5
10
15
20
25
30
time duration (days)
Feed to crackingreactor : atmospheric gasoil
max. allowable outlet temperature of heat exchanger
A
B

0110486

European Patent Office

# EUROPEAN SEARCH REPORT

Application number

EP 83 20 1725

## DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (Int. Cl. 3) |
|---|---|---|---|
| A | FR-A-2 264 261 (SCHMIDTSCHE HEISSDAMPF GESELLSCHAFT)<br>--- | | C 10 G 9/00<br>F 28 F 19/02 |
| A | GB-A- 831 912 (H. SALMEN)<br>--- | | |
| A | US-A-4 054 174 (K.H. HALLER)<br>--- | | |
| A | DE-A-3 038 084 (SUMITOMO)<br>--- | | |
| A | BE-A- 348 252 (COUTURAUD)<br>--- | | |
| A | NL-A-7 007 556 (SHELL)<br>--- | | |
| A | NL-A- 300 760 (SULZER BROTHERS)<br>----- | | |

| TECHNICAL FIELDS SEARCHED (Int. Cl. 3) |
|---|
| C 10 G<br>F 28 F |

The present search report has been drawn up for all claims

| Place of search | Date of completion of the search | Examiner |
|---|---|---|
| THE HAGUE | 13-03-1984 | LO CONTE C. |

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
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