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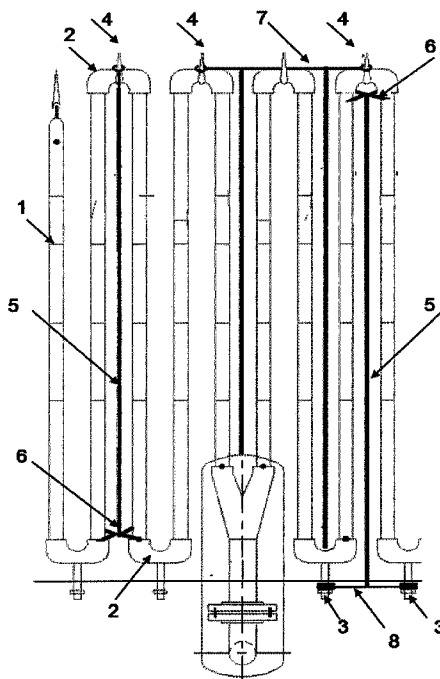
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(54) **Title:** RADIANT FOR USE IN THE RADIANT SECTION OF A FIRED HEATER



(57) **Abrégé/Abstract:**

A substantially linear ceramic or metallic radiant of ellipsoidal or polygonal cross section is placed proximate furnace tubes or coils in the radiant section of a fired heater to increase the radiant heat directed to the surface of the tubes or coils.

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RADIANT FOR USE IN THE RADIANT SECTION OF A FIRED HEATER

ABSTRACT OF THE DISCLOSURE

A substantially linear ceramic or metallic radiant of ellipsoidal or polygonal cross section is placed proximate furnace tubes or coils in the radiant section of a fired heater to increase the radiant heat directed to the surface of the tubes or coils.

RADIANT FOR USE IN THE RADIANT SECTION OF A FIRED HEATER

FIELD OF THE INVENTION

The present invention relates to radiants for use with radiant section tubes in a fired heater, such as furnace tube coils for cracking paraffins such as C₂₋₄ paraffins. The radiant is a substantially linear structure of any cross section, including a ribbon, tube or rod with circular, oval, diamond, rectangular or polygon cross section of a solid (in the phase sense not necessarily a monolith) material having a coefficient of thermal expansion and creep resistance, substantially comparable to the tube coil pass. At a temperature of not less than 1250°C, preferably not less than 1275°C the radiant should have a deformation of up to 100% of the coil pass deformation (e.g. elongation). The radiant absorbs radiant heat from the furnace walls, combustion gasses or both and re-radiates it towards the furnace tube coils. Since the radiant is not cooled by any process fluid, it will have temperature higher than the furnace tube coil which is cooled by the internally flowing process fluid. In petrochemical crackers having vertical or horizontal tube coils, the coils are in a linear array, typically evenly spaced. Radiation from the combustion gases and furnace walls which passes between adjacent tube coils has a lower heating effect on the coils, because the coils are mutually and partially blocking their exposure to the radiating furnace walls and they compete with the adjacent coils for heat radiated by combustion gases passing between them. The radiants between tube coils will capture and redirect radiant energy onto the part of the coil surface which is perpendicular to the furnace walls, e.g. not directly exposed to the refractory walls, and which faces the adjacent coil in the radiant section of the furnace.

Prior Art

U.S. patent 2,733,692 issued Feb 7, 1956 To Sherman assigned to Foster Wheeler teaches an "Oil Heater". The patent appears to relate to refining oil. At the top of the heater the pipes carrying oil pass through the top of the heater. There are
5 passages 45 which are circular to and concentric to the tubes. Heat flows evenly around the entire circumference of the portion of each tube within the passages. Heat is radiated evenly from the wall of each passage to the entire circumference of the tube which it surrounds. (Col. 2 lines 65 -72). The present invention does not contemplate concentric radiative alloy to more evenly distribute radiative heat to
10 furnace tubes.

In a 1965 article, entitled "ETHYLENE", which appeared in the November 13 issue of CHEMICAL WEEK, disclosed some basic discoveries that revolutionized steam cracking furnace design. Researchers discovered that secondary reactions in the reacting gases are responsible for tube-wall coke. Shorter residence time with
15 more heat favors primary olefin-forming reactions, not these secondary coke-causing reactions. Accordingly, higher heat flux and higher tube-wall temperatures emerged as the answer. A shorter residence time requires that heat must be transferred into the hydrocarbons faster. Two feasible ways suggested for expanding this heat input are by altering the mechanical design of the tubes so they have greater external
20 surface per internal volume (i.e. a smaller diameter tube) and increasing the rate of heat flux through the tube walls (a higher temperature). The article did not suggest the use of radiants to increase the wall temperature of the tube nor to improve the uniformity of the circumferential temperature around the tube.

U.S. patent 3,671,198 issued June 20, 1972 to Wallace, assigned to Pullman
25 Incorporated teaches cracking furnaces have smaller diameter vertical cracking

tubes and a quenching system. The patent does not teach or suggest the use of a radiant.

U.S. patent 4,499,055 issued Feb 12, 1985 to DiNicolantonio et al., assigned to Exxon Research and Engineering Company teaches a cracker having vertical
5 furnace tubes in a row. The tubes have a bend so that on thermal expansion they stay in a plane. The patent does not teach or suggest a radiant to improve the efficiency of the radiant section of a cracker.

U.S. patent 8,746,184 issued June 10, 2014 to Horne is the only patent applicants are aware of that discloses the use of radiants. The patent teaches an
10 improved steam boiler using radiants. The radiants are slotted metal sheets through which the combustion gases flow. The radiants are convection heated, not heated by radiation from the walls of the radiant section of the fired heater, and then radiate heat to the pipes to heat water to make steam. This is a change of state application not a change of composition application as in cracking tubes. The patent teaches
15 away from a radiant having a continuous surface (e.g. no slots or holes) and being heated both by convection and by radiation. Further there is no suggestion that the radiants may have any use in the radiant section of a fired heater such as a cracking furnace.

The present invention seeks to provide improved heat transfer efficiency in
20 the radiant section of a chemicals cracker by the use of radiants between the coils. Improved efficiency will lead to a reduction in greenhouse gases from the fired heaters.

SUMMARY OF THE INVENTION

The present invention provides in the radiant section of a fired heater a
25 radiant separate from the walls, having a melting point greater than 1250°C, and

creep and deformation properties comparable to the radiant section tubes in a fired heater, comprising a ceramic or alloy having a continuous surface.

In a further embodiment the present invention provides a radiant in a substantially linear form with a continuous external surface smooth or modified with
5 grooves or covered with micro-protuberances.

In a further embodiment the radiant may be in the form of a ellipsoid or polygon cross-section.

In a further embodiment the total length of a radiant can vary from 25 to 100 % of the length of a tube coil pass in the radiant section of a fired furnace, a
10 thickness sufficient to maintain integrity of the radiant (from 0.5 to 1.5 of the thickness of the furnace coil wall, and width from 1/4 to 3/4 of the external diameter of the furnace tube.

In a further embodiment the present invention provides a radiant having a total length from 50 to 90% of the length of a tube pass in the radiant section of a
15 fired furnace and a diameter from 1/2 to 3/4 of the external diameter of the furnace tube.

In a further embodiment the present invention provides a radiant which is continuous (e.g. unit body).

In a further embodiment the present invention provides a radiant comprising
20 multiple segments joined together.

In a further embodiment at least a portion, typically not less than 25% of the surface of the radiant contains an array of grooves having a depth from 1/16 to 1/8 of the thickness or width or diameter of the radiant.

In a further embodiment the present invention provides a radiant which is
25 vertical.

In a further embodiment the present invention provides a radiant which is horizontal.

In a further embodiment the present invention provides a radiant which is a metallic alloy and has a surface having a thickness from 10 to 5,000 microns
 5 comprising from 40 to 60 weight % of compounds of the formula $Mn_xCr_{3-x}O_4$ wherein x is from 0.5 to 2 and from 60 to 40 weight % of oxides of Mn and Si selected from the group consisting of MnO, MnSiO₃, Mn₂SiO₄ and mixtures thereof provided that the surface contains less than 5 weight % of Cr₂O₃.

In a further embodiment the present invention provides a radiant comprising
 10 from about 55 to 65 weight % of Ni; from about 20 to 10 weight % of Cr; from about 20 to 10 weight % of Co; and from about 5 to 9 weight % of Fe and the balance one or more of the trace elements.

In a further embodiment the present invention provides a radiant further comprising from 0.2 up to 3 weight % of Mn; from 0.3 to 2 weight % of Si; less than 5
 15 weight % of titanium, niobium and all other trace metals; and carbon in an amount of less than 0.75 weight % the sum of the components adding up to 100 weight %.

In a further embodiment the present invention provides a radiant comprising from 40 to 65 weight % of Co; from 15 to 20 weight % of Cr; from 20 to 13 weight % of Ni; less than 4 weight % of Fe and the balance of one or more trace elements and
 20 up to 20 weight % of W the sum of the components adding up to 100 weight %.

In a further embodiment the present invention provides a radiant further comprising from 0.2 up to 3 weight % of Mn; from 0.3 to 2 weight % of Si; less than 5 weight % of titanium, niobium and all other trace metals; and carbon in an amount of less than 0.75 weight %.

In a further embodiment the present invention provides a radiant comprising from 20 to 38 weight % of chromium from 25 to 48, weight % of Ni.

In a further embodiment the present invention provides a radiant further comprising from 0.2 up to 3 weight % of Mn, from 0.3 to 2 weight % of Si; less than 5 weight % of titanium, niobium and all other trace metals; and carbon in an amount of less than 0.75 weight % and the balance substantially iron.

In a further embodiment the present invention provides a radiant comprising an Mo-Si-B alloy.

In a further embodiment the present invention provides a radiant comprising a ceramic selected from the group consisting of silicon dioxide, fused silicon dioxide, aluminum oxide, titanium dioxide, zirconium dioxide, thorium dioxide, lanthanum oxide, magnesium oxide, calcium oxide, barium oxide, tin oxide, cerium dioxide, zinc oxide, boron oxide, boron carbide, yttrium oxide, aluminum silicate, silicon nitride, silicon carbide and mixtures thereof.

In a further embodiment the present invention provides a radiant section of a fired heater having tubes spaced in a pattern in which a coil view factor relative to the wall is altered by presence of an adjacent coil, wherein a radiant as above is positioned proximate at least a pair of adjacent tubes (to increase the radiant energy directed to the surface of said coils).

In a further embodiment the present invention provides a radiant section as above wherein the radiant is vertical.

In a further embodiment the present invention provides a radiant section wherein the radiant is suspended from an overhead mount.

In a further embodiment the present invention provides a radiant section wherein the radiant is floor mounted.

In a further embodiment the present invention provides a radiant section wherein the radiant is horizontal.

In a further embodiment the present invention provides a method of thermally treating a fluid hydrocarbon comprising passing the hydrocarbon through a tube in
5 the radiant section of a fired heater having radiants as above.

In a further embodiment the hydrocarbon is a C₂₋₄ paraffin which is passed through the tubes in the radiant section at a temperature from 800°C to 1100°C for a time from 0.001 to 0.01 seconds.

In a further embodiment the hydrocarbon is selected from the group
10 consisting of heavy crude oil, heavy vacuum gas oil, resid, and naphtha.

In a further embodiment the present invention provides a method to reduce the inhomogeneity of the external and internal circumferential temperature distribution of a tube in the radiant section of a fired heater by placing a radiant proximate the furnace tube

15 In a further embodiment the present invention provides a method to reduce the inhomogeneity of the external and internal circumferential heat flux of a tube in the radiant section of a fired heater by placing a radiant proximate said tube.

A further embodiment of the invention provides a cracking furnace comprising a radiant section having cracking coils spaced in a pattern in which a coil view factor
20 relative to the wall is altered by presence of an adjacent coil, wherein a radiant is positioned proximate at least a pair of adjacent coils to increase the radiant energy directed to the surface of said coils.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic side view of coils and radiants in the radiant section of
25 a furnace, to illustrate how vertical radiant may be installed.

Figure 2 is a schematic sectional view of a corner of a cracking furnace having vertical coils.

Figure 3 is a plot of the circumferential temperature of the right coil in figure 2.

Figure 4 is schematic sectional view of a corner of a cracking furnace having
5 vertical coils and vertical radiants between the coils

Figure 5 is a plot of the circumferential temperature distributions of the right coil from figure 4 and of the right coil from figure 2.

Figure 6 is a plot of the heat fluxes at the inner surface of the right coil from figure 4 and of the right coil from figure 2.

10 Figure 7A is as schematic diagram of a wall fired furnace with the calculated temperature values of the furnace walls and figure 7B is the coil with two adjacent radiants, indicated on Figure 7A, with the calculated temperature values of the inserts and of the coil external wall.

Figure 8 is a schematic of a furnace with ribbon radiants (60), which have a
15 width equal to a diameter of a coil (40).

Figure 9 is a schematic of a furnace with cylindrical radiants (60) which have diameters equal to a diameter of a coil (40).

Figure 10 is a plot showing an increase in heat Q^* absorbed by a coil with adjacent cylindrical and ribbon radiants, respectively, as compared to heat Q
20 absorbed by a coil with no radiants.

DETAILED DESCRIPTION

Numbers ranges

[1] Other than in the operating examples or where otherwise indicated, all numbers or expressions referring to quantities of ingredients, reaction conditions,
25 etc. used in the specification and claims are to be understood as modified in all

instances by the term “about.” Accordingly, unless indicated to the contrary, the numerical parameters set forth in the following specification and attached claims are approximations that can vary depending upon the properties that the present invention desires to obtain. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques.

[2] Notwithstanding that the numerical ranges and parameters setting forth the broad scope of the invention are approximations, the numerical values set forth in the specific examples are reported as precisely as possible. Any numerical values, however, inherently contain certain errors necessarily resulting from the standard deviation found in their respective testing measurements.

[3] Also, it should be understood that any numerical range recited herein is intended to include all sub-ranges subsumed therein. For example, a range of “1 to 10” is intended to include all sub-ranges between and including the recited minimum value of 1 and the recited maximum value of 10; that is, having a minimum value equal to or greater than 1 and a maximum value of equal to or less than 10. Because the disclosed numerical ranges are continuous, they include every value between the minimum and maximum values. Unless expressly indicated otherwise, the various numerical ranges specified in this application are approximations.

[4] All compositional ranges expressed herein are limited in total to and do not exceed 100 percent (volume percent or weight percent) in practice. Where multiple components can be present in a composition, the sum of the maximum amounts of each component can exceed 100 percent, with the understanding that, and as those

skilled in the art readily understand, that the amounts of the components actually used will conform to the maximum of 100 percent.

[5] As used in this specification a view factor ($F_{i,j}$) is defined as the ratio of radiation leaving a surface i that is intercepted by surface j . In a radiant heater, a coil "i" experiences radiation from the furnace walls "w", radiation from adjacent tube coils "j" (which are likely at the same temperature as the considered coil "i", and lower than the wall temperature) and radiation from combustion gases "CG": $F_{i,w}$, $F_{i,coils j}$ and $F_{i,CG}$. This is a three by three matrix. As a practical matter the coils are at substantially the same temperature. When a radiant having a temperature greater than a coil is introduced a new view factor is introduced ($F_{i,(radiant)}$). This creates a four by four matrix for radiant heat transfer to a coil "i", the radiating bodies being the wall, the (adjacent) coils at a lower temperature, the radiants at higher temperature than the coil, and combustion gases at the highest temperature of all.

As used in this specification a "radiant" means a structure having a closed surface (no slots), smooth or extended with grooves or micro-protuberances, made of a material having a melting temperature above 1250 ° C, preferably greater than 1275°C. The radiant may be in the form of a ribbon, tube or rod with circular, oval, triangular, rectangular, diamond-shaped or polygon cross-section. It can comprise one segment of the required length or multiple segments which are joint together to form a radiant of the required length.

There are a number of chemical processes in which a hydrocarbon is subject to a heat treatment. In many of these treatments the hydrocarbon is passed in liquid or gaseous form through a tube or furnace coil in the radiant section of fired heater (or radiant section tubes or coils of a fired heater). The hydrocarbon may be diluted by steam. Such treatments include cracking of paraffins such as naphtha and lower

C₂₋₄ paraffins to form olefins. Other treatments include the processing of crude oil, including heavy crude oil, heavy vacuum gas, and the residual fraction from the vacuum separation of a thermally treated (heavy) crude oil and various forms of coking (delayed coking, FLEXICOKING™, and visbreaking). Radiants may be used
5 in any process involving the radiant transfer of heat to a tube or coil containing a hydrocarbon to be processed. One particularly useful application of radiants in the radiant section of a fired heater is to crack paraffins to olefins such as cracking naphtha or lower C₂₋₄ paraffins to olefins.

Thermal treatment of hydrocarbons as reference above is an energy intensive
10 process. The hydrocarbon feed passes through a number of pipes or coils in the convection and radiant sections of fired heater (i.e. a furnace). In the radiant section of the furnace there are burners typically in the walls but they may also be floor mounted. The walls in the radiant section comprise refractory material such as brick. Fuel, such as e.g. natural gas, is fed to the burners. The combustion gasses from
15 the burners rise through the radiant section. The walls of the radiant section are heated and generate radiation to heat the coils in the radiant section. Additionally as the combustion gasses rise through the radiant section they provide radiation and convection heating to the coils heating their contents the required temperature such as a cracking temperature. Cracking temperatures may range from at least 800°C to
20 about 1100 °C, preferably at least about 900 °C to about 1100 °C, typically from 950°C to 1050 °C. Other thermal treatments may take place over a broader temperature range such as from 500° C to 1200° C, typically from 600° to 1150° C. The time for the thermal treatment may range from mili-seconds (0.001 seconds) to 1 second typically from 0.001 to 0.1 seconds, in some embodiments from 0.001 to
25 0.01 seconds. Generally the thermal treatments may be carried out at low pressures,

in some cases near atmospheric pressure (e.g. from 80 kPa to about 120 kPa). The product stream is then separated in a conventional manner.

Typically the combustion gasses exiting from the radiant section pass through the convection section of the furnace passing over tubes or coils to pre-heat their content to near cracking temperature. The gasses then exit the convection section, flow through the stack and exit the furnace.

In the radiant section of the furnace, the coils may be vertical or horizontal. Typically there are two or more arrays of furnace coils spaced on either side of the furnace proximate the wall. The coils typically comprise straight passes connected by "U" bends to provide a continuous flow path for the feed. The straight passes are spaced apart typically from about $\frac{1}{2}$ to 2, generally from about $\frac{1}{2}$ to 1 $\frac{1}{2}$ times the diameter of the pass. The radiation from the furnace walls impinges on the side of the coil exposed/ adjacent to the wall. Between the coil passes there is nothing to "catch" the radiation from the wall and to redirect it to the coils. There is a shadow area cast by one coil on an adjacent coil where radiation from the walls is partially blocked. As a result, there is less heat radiated on the side of coil surface which faces the other coil and, as a result, the coils do not have a uniform circumferential surface temperature.

A radiant may be placed typically approximately equidistant between the straight passes of the coils. The radiant is heated by the radiation from the walls of the furnace radiant section and also, it is heated by the combustion gasses. The radiant then radiates energy to the sides of the furnace tubes facing it. This results in a more uniform circumferential temperature distribution in the coil and an increase in the total heat transferred to the coil. The radiant should have a continuous external surface.

Optionally at least a portion typically 25%, preferably greater than 50% of the surface of the radiant may have a pattern of grooves or protuberances. The grooves may have a depth from 1/16 to 1/8 of the thickness or diameter of the radiant. The grooves may be in the form of an outwardly open V, a truncated outwardly open V, an outwardly open U, an outwardly open parallel sided channel. The protuberances may be evenly or unevenly spaced along the radiant. The proximity of the protuberances to each other may change along the length of the radiant. The protuberances may comprise from 5% up to 35% of the weight of the radiant. The protuberance may have geometrical shape, having a relatively large external surface that contains a relatively small volume, such as for example tetrahedrons, pyramids, cubes, cones, a section through a sphere (e.g. hemispherical or less), a section through an ellipsoid, a section through a deformed ellipsoid (e.g. a tear drop) etc. Some useful shapes for a protuberance include:

a tetrahedron (pyramid with a triangular base and 3 faces that are equilateral triangles);

a Johnson square pyramid (pyramid with a square base and sides which are equilateral triangles);

a pyramid with 4 isosceles triangle sides;

a pyramid with isosceles triangle sides (e.g. if it is a four faced pyramid the base may not be a square it could be a rectangle or a parallelogram);

a section of a sphere (e.g. a hemisphere or less);

a section of an ellipsoid (e.g. a section through the shape or volume formed when an ellipse is rotated through its major or minor axis); and.

a section of a tear drop (e.g. a section through the shape or volume formed when a non uniformly deformed ellipsoid is rotated along the axis of deformation);

a section of a parabola (e.g. section through the shape or volume formed when a parabola is rotated about its major axis – a deformed hemi- (or less) sphere)

The radiant may be hollow or solid provided it has sufficient mechanical stability to withstand the environment. The radiants will be subject to thermal stress and will to some extent undergo deformation (length change). It should be noted that some shapes such as a ribbon or bar when under non uniform thermal stress may be more prone to warping or bending.

The radiant may have a dimensions from about at least 75 %, in some instances at least 80 %, desirably at least 90 %, preferably 100% of the length of the tube pass within the radiant section. For a bar or a ribbon the radiant may have a thickness from 0.5 to 1.5 of the thickness of the tube wall and a width from $\frac{3}{8}$ to $\frac{7}{8}$, desirably from $\frac{1}{2}$ to $\frac{3}{4}$ of the external diameter of the furnace tube. For tubular radiants the diameter may be from $\frac{2}{8}$ to $\frac{7}{8}$, desirably from $\frac{1}{2}$ to $\frac{3}{4}$ of the external diameter of the furnace tube. The width (or diameter for a circular radiant) is based on the coil or pipe exposure to the refractory and other coils. The radiant should be wide enough to shield the tube or coil from exchanging heat with adjacent coils, but small enough not to reduce the coil or tube view factor with respect to the furnace wall refractory. One advantage of a tubular radiant is that it may be less prone to bending or warping in use.

The radiant may be made of any material capable of withstanding the ambient conditions in the radiant section of the cracking furnace. The radiant may be metallic or ceramic. The radiant should have an emissivity greater than 0.5, typically from 0.6 to 0.95, desirably from 0.6 to 0.85, preferably from 0.6 to 0.8 in some embodiments from 0.6 to 0.7.

The radiant may be stainless steel which may be selected from the group consisting of wrought stainless, austentic stainless steel and HP, HT, HU, HW and HX stainless steel, heat resistant steel, and nickel or molybdenum based alloys (thermalloy). The radiant may be a high strength low alloy steel (HSLA); high
 5 strength structural steel or ultra high strength steel. The classification and composition of such steels are known to those skilled in the art.

In one embodiment, the stainless steel, preferably heat resistant stainless steel typically comprises from 13 to 50, preferably 20 to 50, most preferably from 20 to 38 weight % of chromium. The stainless steel may further comprise from 20 to 50,
 10 preferably from 25 to 50 most preferably from 25 to 48, desirably from about 30 to 45 weight % of Ni. The balance of the stainless steel may be substantially iron.

The present invention may also be used with nickel and/or cobalt based extreme austentic high temperature alloys (HTAs). Typically, the alloys comprise a major amount of nickel or cobalt. Typically, the high temperature nickel based alloys
 15 comprise from about 50 to 70, preferably from about 55 to 65 weight % of Ni; from about 20 to 10 weight % of Cr; from about 20 to 10 weight % of Co; and from about 5 to 9 weight % of Fe and the balance one or more of the trace elements noted below to bring the composition up to 100 weight %. Typically, the high temperature cobalt based alloys comprise from 40 to 65 weight % of Co; from 15 to 20 weight % of Cr;
 20 from 20 to 13 weight % of Ni; less than 4 weight % of Fe and the balance one or more trace elements as set out below and up to 20 weight % of W. The sum of the components adding up to 100 weight %.

In some embodiments of the invention, the steel may further comprise a number of trace elements including at least 0.2 weight %, up to 3 weight % typically
 25 1.0 weight %, up to 2.5 weight % preferably not more than 2 weight % of

manganese; from 0.3 to 2, preferably 0.8 to 1.6 typically less than 1.9 weight % of Si; less than 3, typically less than 2 weight % of titanium, niobium (typically less than 2.0, preferably less than 1.5 weight % of niobium) and all other trace metals; and carbon in an amount of less than 2.0 weight %. The trace elements are present
5 in amounts so that the composition of the steel totals 100 weight %.

Newer alloys may be used which contain up to about 12% Al, typically less than 7 weight %, generally about 2.5 to 3 weight % aluminum as disclosed for example in United States Patent 7,278,828 issued October 9, 2007 to Steplewski et al., assigned to General Electric Company. Typically, in the high cobalt and high
10 nickel steels the aluminum may be present in an amount up to 3 weight %, typically between 2.5 and 3 weight %. In the high chrome high nickel alloys (e.g. 13 to 50, preferably 20 to 50, weight % of Cr and from 20 to 50 weight % of Ni) the aluminum content may range up to 10, preferably less than about 7, typically from about 2 to 7 weight %.

15 For high chrome steels the radiant may have has a surface having a thickness from 10 to 5,000 microns comprising from 40 to 60 weight % of compounds of the formula $Mn_xCr_{3-x}O_4$ wherein x is from 0.5 to 2 and from 60 to 40 weight % of oxides of Mn and Si selected from the group consisting of MnO, MnSiO₃, Mn₂SiO₄ and mixtures thereof provided that the surface contains less than 5 weight % of Cr₂O₃.

20 The radiant may be an alloy of molybdenum and silica optionally containing boron (e.g. MoSi₂ or Mo₅SiB₂).

Such surfaces may be produced using a treatment disclosed in United States Patent 6,436,202 issued Aug. 20, 2002 to Benum et al., assigned to NOVA Chemicals (International) S.A.

The radiant may be a ceramic. Some ceramics are capable of withstanding the high temperatures in the radiant section of the furnace. However ceramics tend to be brittle. The ductility of the matrix may be improved by incorporating metallic or ceramic platelets, whiskers having a high aspect ratio or particles into the ceramic body (ceramic matrix composite- CMC). Typically the body of the ceramic may comprise an oxide, carbide, nitride or borate including silicon dioxide, fused silicon dioxide, aluminum oxide, titanium dioxide, zirconium dioxide, thorium dioxide, lanthanum oxide, magnesium oxide, calcium oxide, barium oxide, tin oxide, cerium dioxide, zinc oxide, boron oxide, boron carbide, yttrium oxide, aluminum silicate, silicon nitride, silicon carbide hafnium boride, zirconium boride, tantalum boride, tantalum carbide, titanium boride, tantalum carbide, hafnium carbide, niobium carbide, titanium carbide, zirconium carbide, hafnium nitride, tantalum nitride and zirconium nitride, and mixtures thereof.

The fibers or whiskers, platelets, or particles may be selected from the group consisting of silicon carbide, silicon nitride, boron carbide and boron nitride. In some instances metals having a high melting point may be use. The reinforcing material may be coated with a very thin coating (1-5 microns) of a substance to permit some "slippage" of the reinforcement in the ceramic to reduce crack propagation (e.g. carbon).

U.S. patent application 2010/0081556 published April 1, 2010 to Heng at al., and U.S. Patent 8,409,491 issued April 2, 2013 to Stackpoole et al., assigned to The United States of America as represented by the Administration of the National Aeronautics & Space Administration (NASA), the contents of which are useful in describing high temperature ceramics having good tensile properties.

The radiant whether metal (e.g. steel or thermalloy) or ceramic typically has a thermal emissivity between 0.6 and 0.8.

The radiant may be vertical spaced approximately (e.g. within about 20%, preferably about 10% or less from the midpoint) equidistant between adjacent
 5 furnace tubes. Figure 1 schematically shows how the radiant may be fixed in the radiant section of a furnace having vertical tubes or coils. In figure 1 the furnace tubes or coils 1, which may be formed from a number of sections form a series of straight passes joined at the top and bottom by "U" bends 2. The coil may be anchored in the radiant section of the furnace by supports at the "U" bends at the
 10 bottom of the furnace or supports 3 or hangers 4 at the top of the furnace. A radiant 5 may be hung directly from the support (hanger) 4 at the top of the "U" bend. Spacers- separators 6 may be used to keep the radiant in position and reduce thermal bending or flexing. A stringer 7 may be joined to two or more hangers 4, and one or more radiants 5 may be hung from the stringer 7. A stringer 8 may also run
 15 between one or more bottom guides 3 s and a radiant 5 may be supported from the bottom stringer. The bottom supported radiant 5 may also have spacers 6 to help position the radiant 5 and reduce thermal bending and flexing.

The radiant may be suspended from upper part of the radiant section such as the supports for the roof or the under surface of the roof per se. Suitable mechanical
 20 couplings and suspending devices are known to one of ordinary skill in the art. A vertical radiant could be supported directly or indirectly (stringers or guides) from the floor of the radiant section and the hangers for the coils. In some embodiments, a vertical radiant could be supported from both the floor and the hangers for the coils in the upper part of the radiant section of the furnace.

Horizontal radiants could be supported from the upper section or the floor or both of the radiant section of the furnace. In an alternative embodiment, the horizontal radiants could be supported from the end walls of the radiant sections or stringers running from the upper portions (ceiling) to the floor of the radiant section.

- 5 Suitable mechanical couplings and suspending devices are known to one of ordinary skill in the art.

The present invention will now be illustrated by the following non limiting examples.

Reference case: Model of the Radiant Section of the Cracking Furnace.

- 10 A computer model of the heat transfer in the radiant section of the NOVA Chemicals second ethane cracker at Joffre was developed, using ANSYS Mechanical software. The model was run to simulate the process in the cracking furnace in which there were no radiants between the vertical coils in the furnace radiant section. The coils were heated by radiation from the furnace walls and by
15 forced convection by combustion gases produced by the furnace wall burners and flowing along the coils. Heat acquired by the coil external surface was transferred by conduction through the coil wall and by internal forced convection to the stream of process gas (feed) flowing inside the coil. The model predicted the temperature of the external and internal surfaces of the coils, as well as temperature of furnace
20 refractory. The input data used for the simulation, such as specific geometry and dimensions of the furnace and of the coils, feed flow rate, fuel gas composition and flow rate into the burners, feed and product compositions and temperatures at the inlet and outlet of the furnace radiant section, etc, were the actual operating data measured in the cracking furnace in Joffre. There was good qualitative agreement

between the calculated and the measured coil surface temperatures, and the model validly represented the operation of the furnace radiant section.

In the figures, like parts are designated by like reference numbers.

Figure 2 shows a schematic cross section of the furnace tube coils in a furnace. In figure 2, the furnace is generally indicated as 20, the furnace walls 10 radiate heat generated by the burners 30 onto the coils 40. The cooler coil surface area due to a reduced view factor due to adjacent coils is referenced by 50. Figure 3 shows the temperature distribution around the half of the coil circumference (180°), with the maximum temperature corresponding to the coil surface exposed directly to the furnace walls, and the lowest coil temperature on the coil side facing the adjacent coils.

Figure 6 is a plot of the heat flux around the internal surface of a coil 40 when radiants are absent (i.e. figure 2) and when radiants 60 are present (i.e. figure 4).

Example 1.

The simulation was re-run except that a radiant was placed at the center point between the tubes, as shown in Figure 4 is a schematic view of a furnace having radiants 60 placed between the coils 40. In figure 4 the dark area 70 is the heat radiated by the radiants 60 to the surface of coil 40.

The radiant was a ribbon having the same radiative emissivity as the coils. The radiant had the same length as the coil pass. Apart from the radiants, the conditions of the simulation were kept constant. Figure 5 plots of the circumferential temperature distribution in the coil of the reference case (no radiants, as in Figure 2) and in the case where radiants are present (i.e. Figure 4). The plot shows that there is a more uniform circumferential temperature on the coil surface in the case where radiants are present.

The resulting heat flux absorbed by coils with and without radiants is shown in figure 6. Figure 6 shows that the heat flux arriving to the internal surface of a coil 40 when radiants are absent (i.e. figure 2) is lower than when the radiants 60 are present (i.e. figure 4).

5 As there is no fluid flowing through the radiant it reaches a higher temperature than the tube or coil and radiates heat towards the adjacent coils. The calculated temperature distribution in the furnace walls 10, coils 40 and radiants 60 are shown for a side wall fired furnace in Figures 7A and 7B. The figures show that the radiants 60 are at higher temperature than the coils 40 and that radiant 60 temperature is
10 very close to temperature of furnace end walls with no burners. This shows that for bottom fired heaters or furnaces, when burners are not installed on the walls, temperatures of all furnace walls should be similar, and the temperature of the radiants should be close to the temperature of the walls.

Example 2.

15 The simulation was re-run except there were no radiants but the furnace coils had two longitudinal fins parallel to the side walls of the radiant section. The fins were made of the same material as coils, thus, had the same properties such as emissivity and conductivity as the coil (and the radiant). The radiant heat transmission to the finned coils was slightly higher (by 1. 0% -2.0%) than for the case
20 when coils were bare but separated by radiants. However, contrary to the radiants, the finned coils are much more expensive, challenging to manufacture and are subjected to a creep strain.

Example 3

The analytical model of radiation in the furnace, comprising coils and radiants
25 was developed. Two radiant geometries were considered: a ribbon and a cylinder.

The temperature of the furnace walls and of the coils were assumed as in the ANSYS model (i.e. $T_{\text{wall}}=1170^{\circ}\text{C}$, $T_{\text{coil}}=940^{\circ}\text{C}$) and so were the respective emissivities (i.e. coil emissivity =0.8, radiant emissivity =0.8, furnace wall emissivity =0.6). The view factors were calculated rigorously for the coils separated with the ribbon and cylindrical radiants. To simplify the complexity of the radiation pattern in a furnace with radiants, it has been assumed that the width of the ribbon radiants (60) was equal to the diameter of the coils (40), as shown in Figure 8 and so was the diameter of cylindrical radiants (60), as shown in Figure 9.

Heat received by a coil Q^* separated by both types of radiants was calculated as a function of radiant temperature and was compared with heat Q received by a coil with no radiants. The results, shown in Figure 10, indicate that the benefit of the cylindrical radiant was larger than the benefit of the ribbon radiant. The calculation demonstrates the trends only, not a practical applications, as both radiants are assumed to be of a size of coil diameter.

The shaded area in figure 10 shows that a ribbon radiant to be efficient has to be heated to temperature $>1040^{\circ}\text{C}$, (i.e. $Q^*/Q>1$ for $t>1040^{\circ}\text{C}$), while a cylindrical radiant is already efficient when its temperature exceeds 975°C (i.e. $Q^*/Q>1$ for $t>975^{\circ}\text{C}$).

An additional benefit of a cylindrical radiant can be a lower thermal stress on the cylindrical radiant and less tendency of the radiant to warp or bend.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A radiant, in the radiant section of a fired heater having at least one furnace tube for carrying hydrocarbons, separate from the walls of the fired heater, having a melting point greater than 1250°C, creep and deformation properties comparable to the tubes for carrying hydrocarbons, and comprising a ceramic or alloy having a continuous surface.
2. The radiant according to claim 1, in the form of a substantially linear element with cross section of ellipsoid or polygon.
3. The radiant according to claim 1, having an external surface which is smooth or modified with grooves or micro-protuberances.
4. The radiant according to claim 1, comprising a continuous element.
5. The radiant according to claim 1, comprising multiple joined segments.
6. The radiant according to claim 4, having a length from 25 to 100% of the length of a tube pass in the radiant section of a fired heater.
7. The radiant according to claim 5, having a length from 25 to 100% of the length of a tube pass in the radiant section of a fired heater.

8. The radiant according to claim 6, having a length from 50 to 90% of the length of a tube pass in the radiant section of a fired heater and a diameter from 1/4 to 3/4 of the external diameter of the furnace tube.
9. The radiant according to claim 7, having a length from 50 to 90% of the length of a tube pass in the radiant section of a fired heater and a diameter from 1/4 to 3/4 of the external diameter of the furnace tube.
10. The radiant according to claim 8, which is vertical.
11. The radiant according to claim 9, which is horizontal.
12. The radiant according to claim 4 which is an alloy and has a surface having a thickness from 10 to 5,000 microns comprising from 40 to 60 weight % of compounds of the formula $Mn_xCr_{3-x}O_4$ wherein x is from 0.5 to 2 and from 60 to 40 weight % of oxides of Mn and Si selected from the group consisting of MnO, $MnSiO_3$, Mn_2SiO_4 and mixtures thereof provided that the surface contains less than 5 weight % of Cr_2O_3 .
13. The radiant according to claim 4, comprising from about 55 to about 65 weight % of Ni; from about 20 to about 10 weight % of Cr; from about 20 to about 10 weight % of Co; and from about 5 to about 9 weight % of Fe and the balance one or more of trace elements.

14. The radiant according to claim 13, further comprising from 0.2 up to 3 weight % of Mn; from 0.3 to 2 weight % of Si; less than 5 weight % of titanium, niobium and all other trace metals; and carbon in an amount of less than 0.75 weight % the sum of the components adding up to 100 weight %.

15. The radiant according to claim 4, comprising from 40 to 65 weight % of Co; from 15 to 20 weight % of Cr; from 20 to 13 weight % of Ni; less than 4 weight % of Fe and the balance of one or more trace elements and up to 20 weight % of W the sum of the components adding up to 100 weight %.

16. The radiant according to claim 15, further comprising from 0.2 up to 3 weight % of Mn; from 0.3 to 2 weight % of Si; less than 5 weight % of titanium, niobium and all other trace metals; and carbon in an amount of less than 0.75 weight %.

17. The radiant according to claim 4, comprising from 20 to 38 weight % of chromium from 25 to 48, weight % of Ni.

18 The radiant according to claim 17, further comprising from 0.2 up to 3 weight % of Mn, from 0.3 to 2 weight % of Si; less than 5 weight % of titanium, niobium and all other trace metals; and carbon in an amount of less than 0.75 weight % and the balance substantially iron.

19. The radiant according to claim 4, comprising a ceramic selected from the group consisting of silicon dioxide, fused silicon dioxide, aluminum oxide,

titanium dioxide, zirconium dioxide, thorium dioxide, lanthanum oxide, magnesium oxide, calcium oxide, barium oxide, tin oxide, cerium dioxide, zinc oxide, boron oxide, boron carbide, yttrium oxide, aluminum silicate, silicon nitride, silicon carbide and mixtures thereof.

20. The radiant according to claim 5, which is an alloy and has a surface having a thickness from 10 to 5,000 microns comprising from 40 to 60 weight % of compounds of the formula $Mn_xCr_{3-x}O_4$ wherein x is from 0.5 to 2 and from 60 to 40 weight % of oxides of Mn and Si selected from the group consisting of MnO, MnSiO₃, Mn₂SiO₄ and mixtures thereof provided that the surface contains less than 5 weight % of Cr₂O₃.

21. The radiant according to claim 5, comprising from about 55 to about 65 weight % of Ni; from about 20 to about 10 weight % of Cr; from about 20 to about 10 weight % of Co; and from about 5 to about 9 weight % of Fe and the balance one or more trace elements.

22. The radiant according to claim 21, further comprising from 0.2 up to 3 weight % of Mn; from 0.3 to 2 weight % of Si; less than 5 weight % of titanium, niobium and all other trace metals; and carbon in an amount of less than 0.75 weight % the sum of the components adding up to 100 weight %.

23. The radiant according to claim 5, comprising from 40 to 65 weight % of Co; from 15 to 20 weight % of Cr; from 20 to 13 weight % of Ni; less than 4

weight % of Fe and the balance of one or more trace elements and up to 20 weight % of W the sum of the components adding up to 100 weight %.

24. The radiant according to claim 23, further comprising from 0.2 up to 3 weight % of Mn; from 0.3 to 2 weight % of Si; less than 5 weight % of titanium, niobium and all other trace metals; and carbon in an amount of less than 0.75 weight %.

25. The radiant according to claim 5, comprising from 20 to 38 weight % of chromium from 25 to 48, weight % of Ni.

26. The radiant according to claim 25, further comprising from 0.2 up to 3 weight % of Mn, from 0.3 to 2 weight % of Si; less than 5 weight % of titanium, niobium and all other trace metals; and carbon in an amount of less than 0.75 weight % and the balance substantially iron.

27. The radiant according to claim 5, comprising an alloy of molybdenum and silica optionally containing boron.

28. The radiant according to claim 5, comprising a ceramic selected from the group consisting of consisting of silicon dioxide, fused silicon dioxide, aluminum oxide, titanium dioxide, zirconium dioxide, thorium dioxide, lanthanum oxide, magnesium oxide, calcium oxide, barium oxide, tin oxide, cerium dioxide, zinc oxide, boron oxide, boron carbide, yttrium oxide, aluminum silicate, silicon nitride, silicon carbide and mixtures thereof.

29. A radiant section of a fired heater having tubes spaced in a pattern where a tube view factor is altered by presence of an adjacent tube, wherein at least one radiant according to claim 1 is positioned proximate at least a pair of tubes to increase the radiant energy directed to the surface of said tubes.

30. The radiant section of a fired heater according to claim 29, wherein the radiant is vertical.

31. The radiant section of a fired heater according to claim 30, wherein the radiant is suspended from an overhead mount.

32. The radiant section of a fired heater to claim 30, wherein the radiant is floor mounted.

33. The radiant section of a fired heater according to claim 30, wherein the radiant is supported by links attached to coils.

34. The radiant section of a fired heater to claim 29, wherein the radiant is horizontal.

35. A method of thermally treating a fluid hydrocarbon comprising passing the hydrocarbon through the radiant section of a fired heater according to claim 30, at a temperature from 800°C to 1100°C.

36. A method of thermally treating a fluid hydrocarbon comprising passing the hydrocarbon through the radiant section of a fired heater according to claim 34, at a temperature from 800°C to 1100°C.
37. The method according to claim 35, wherein the hydrocarbon is selected from the group consisting of naphtha and C₂₋₄ paraffins and the time of treatment is from 0.001 seconds to 0.1 seconds.
38. The method according to claim 36, wherein the hydrocarbon is selected from the group consisting of naphtha and C₂₋₄ paraffins and the time of treatment is from 0.001seconds to 01 seconds.
39. A method to improve the uniformity of circumferential temperature distribution in a tube in the radiant section of a fired heater comprising placing a radiant according to claim 1 adjacent said tube.
40. A method to improve the uniformity of circumferential heat flux to a tube in the radiant section of a fired heater comprising placing a radiant according to claim 1 adjacent said tube.
41. A cracking furnace comprising a radiant section having cracking coils spaced in a pattern in which a coil view factor relative to the wall is altered by presence of an adjacent coil, wherein a radiant according to claim 1, is position proximate at least a pair of adjacent coils to increase the radiant energy directed to the surface of said coils.

Figure 1

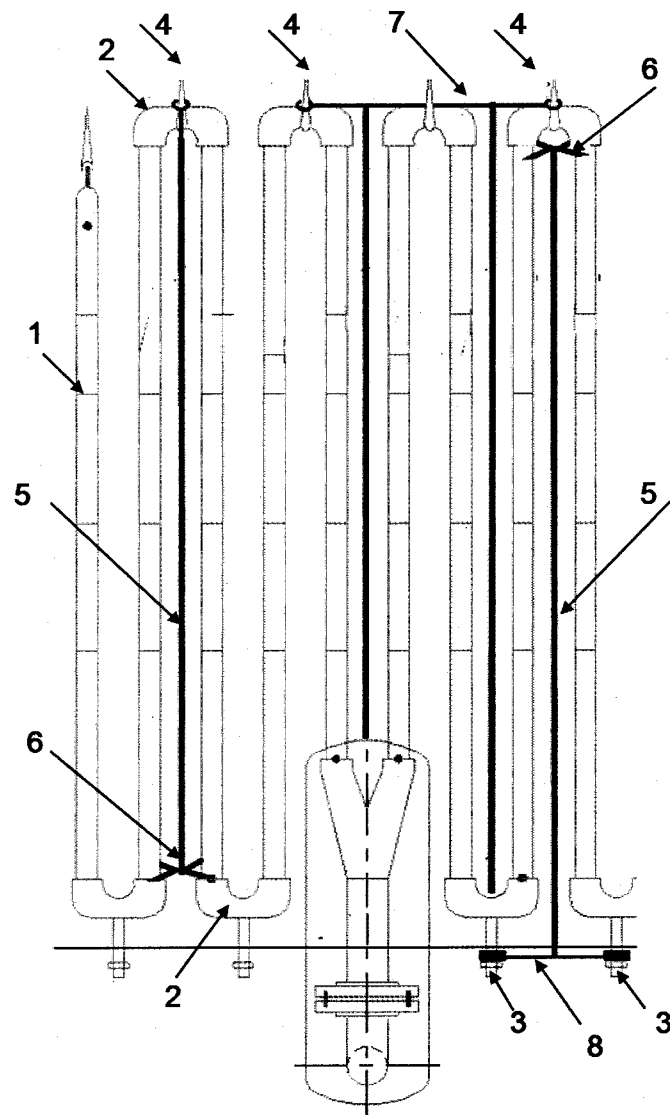


Figure 2

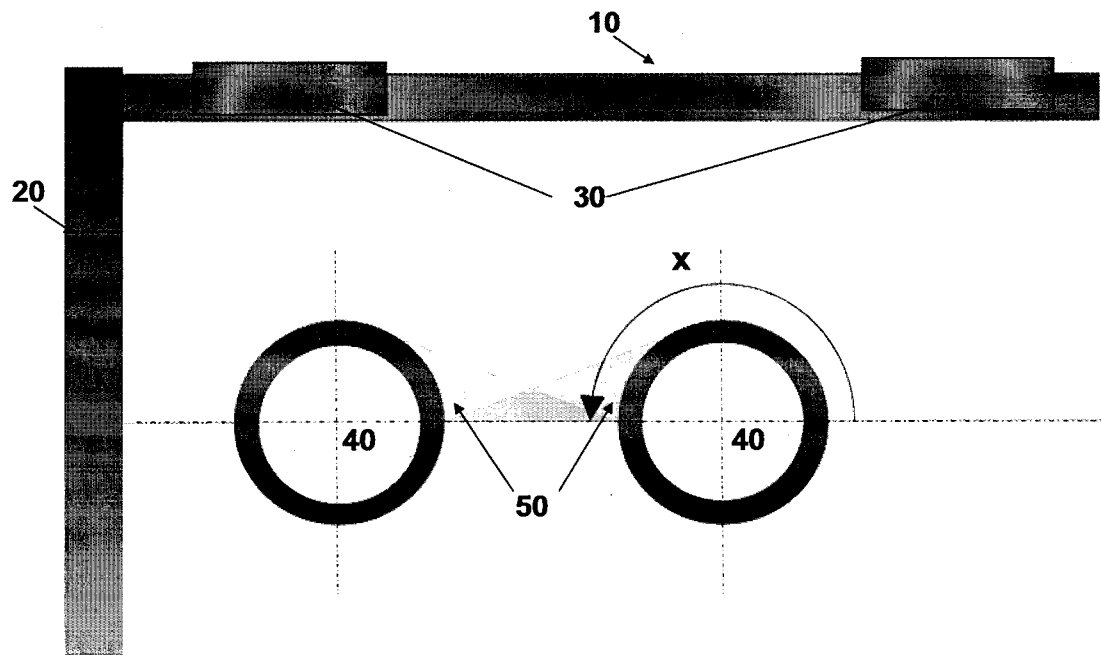


Figure 3

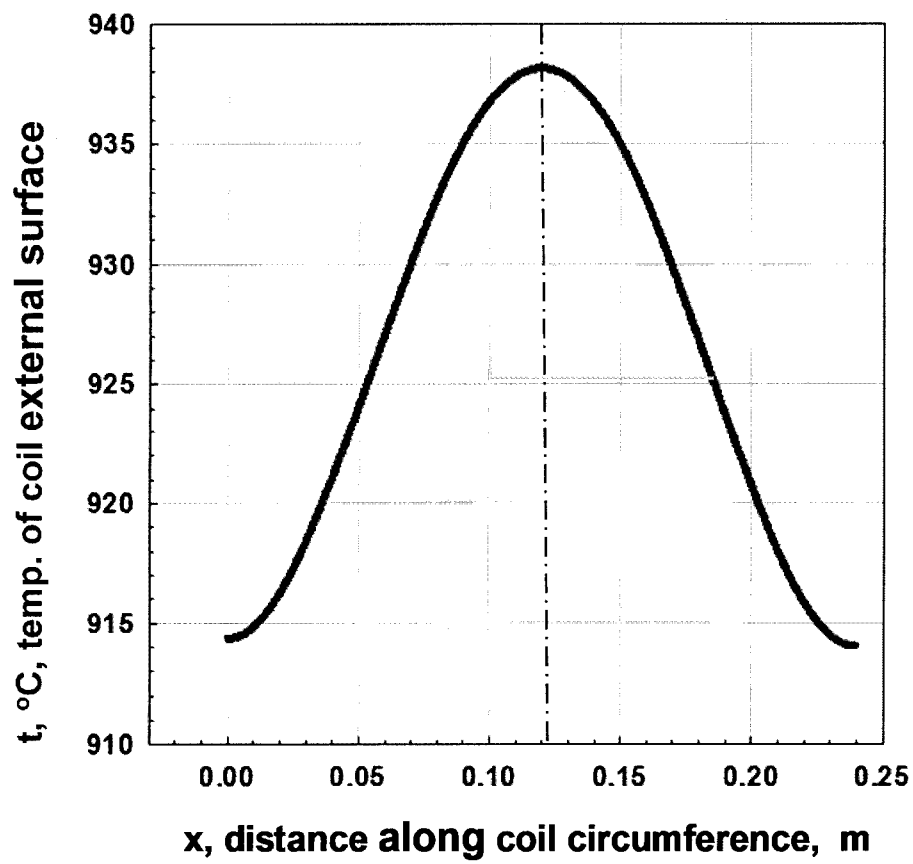


Figure 4

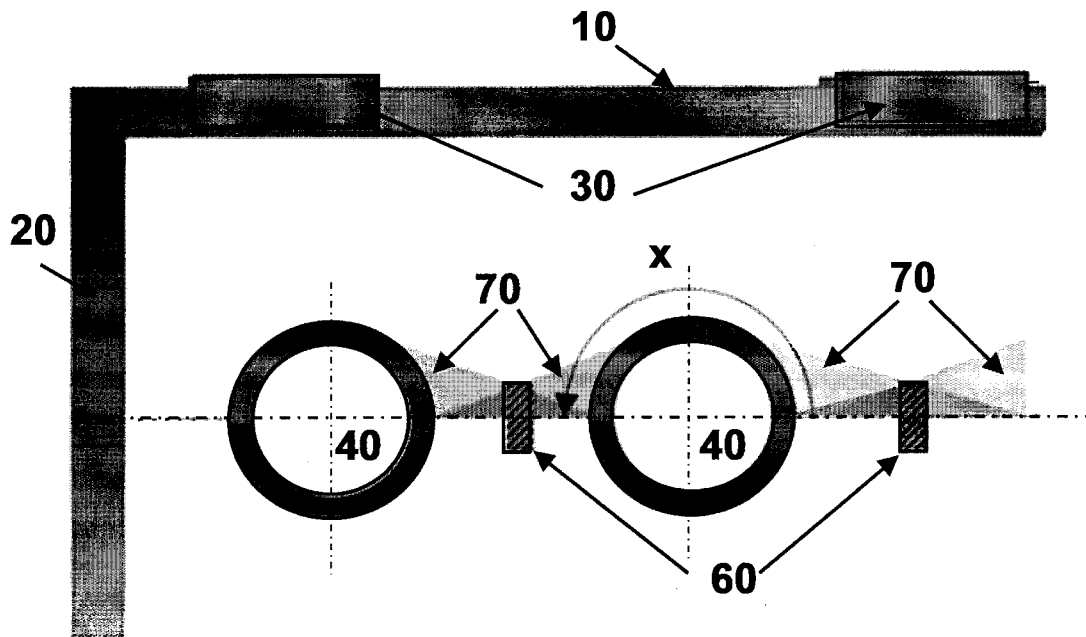


Figure 5

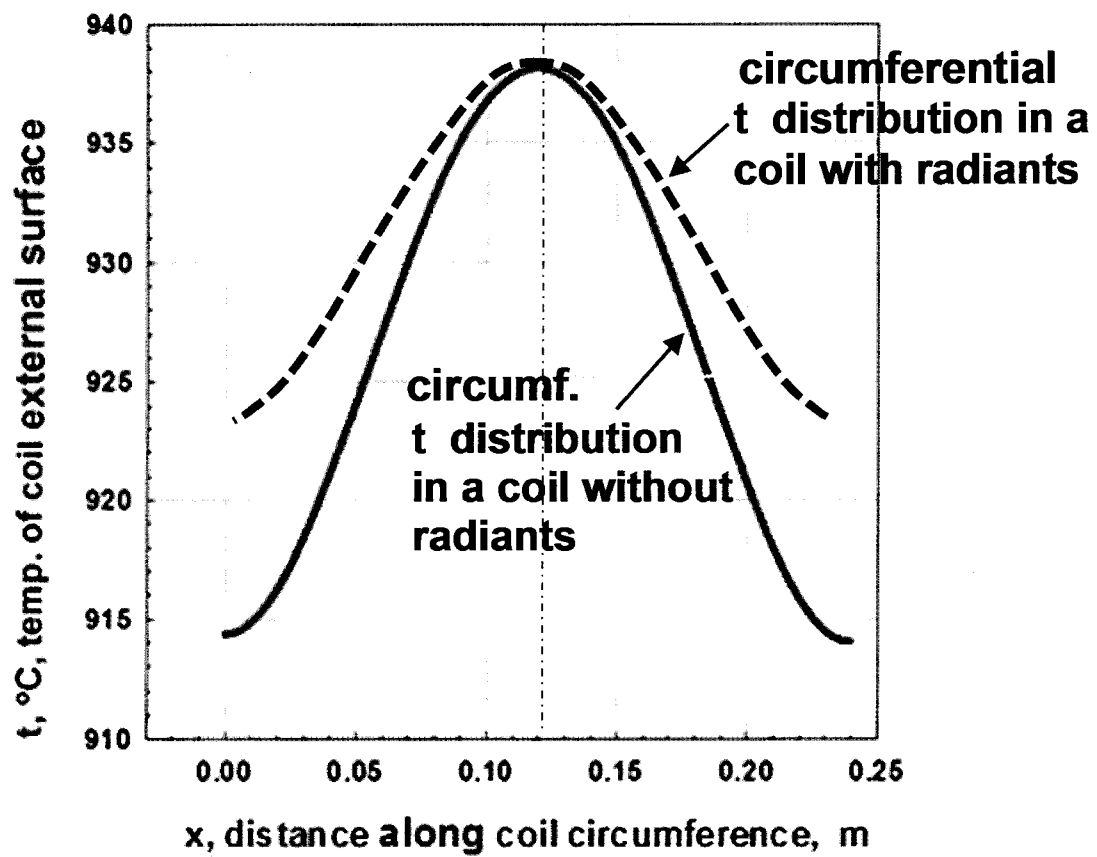


Figure 6

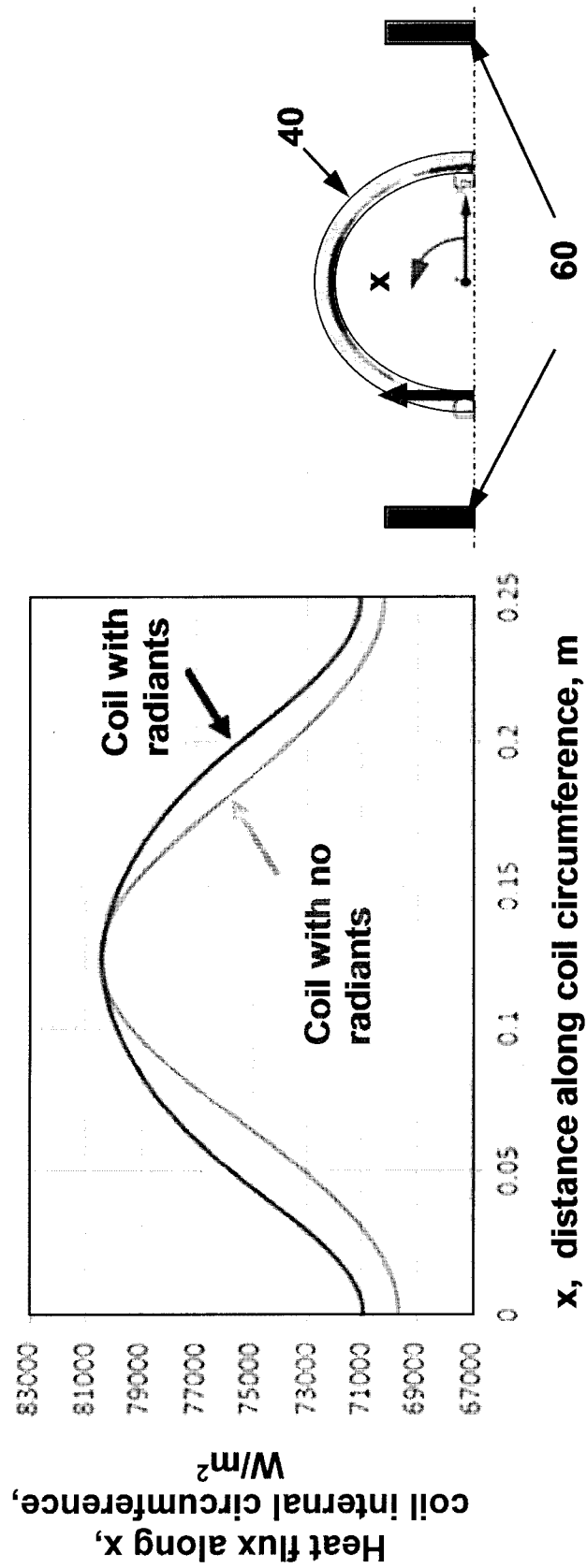


Figure 7A

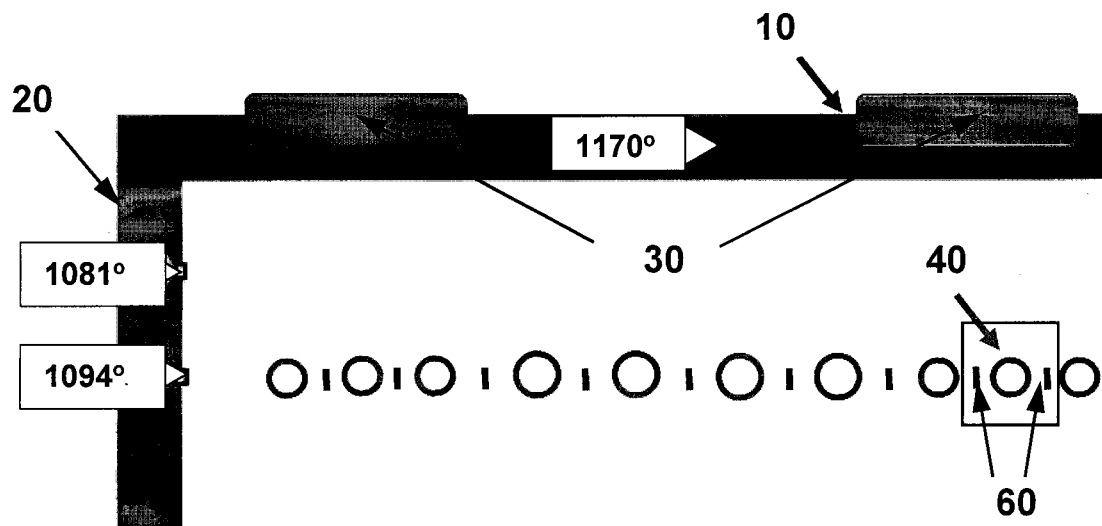


Figure 7B

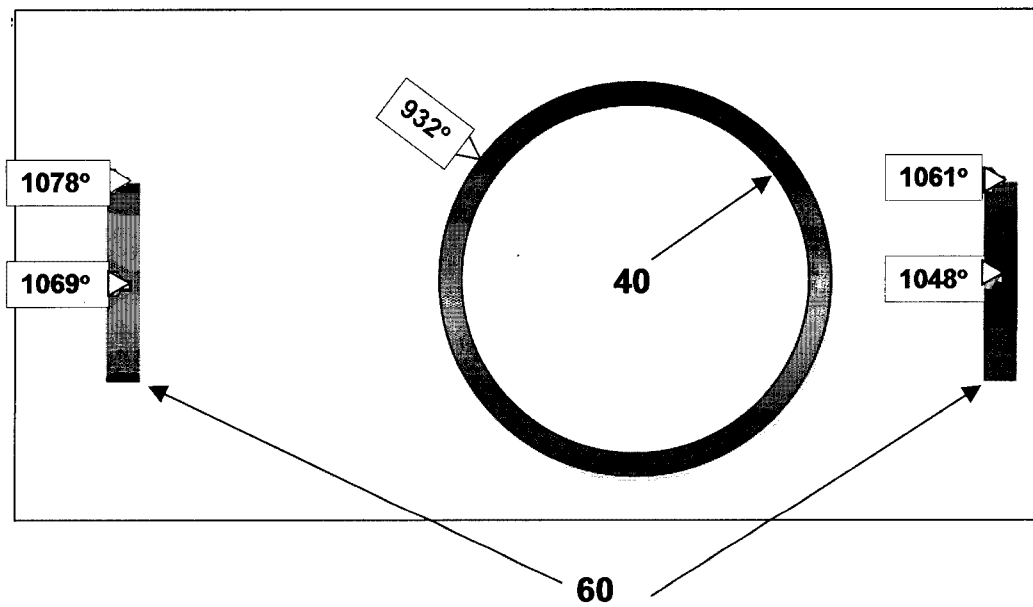


Figure 8

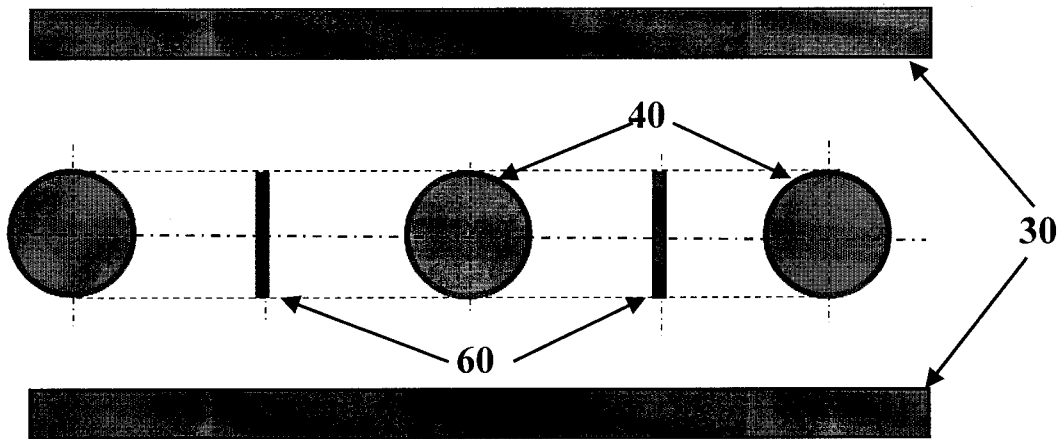


Figure 9

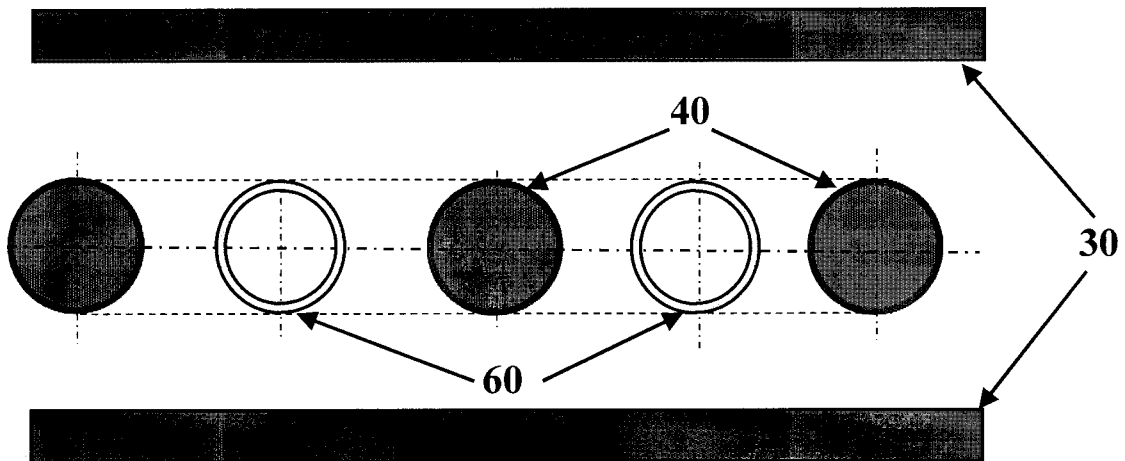


Figure 10

