Sept. 18, 1945. C. H. THAYER ET AL 2,384,858

TEMPERATURE CONTROL OF CONTACTING REACTIONS

Filed Dec. 6, 1941 2 Sheets-Sheet 1

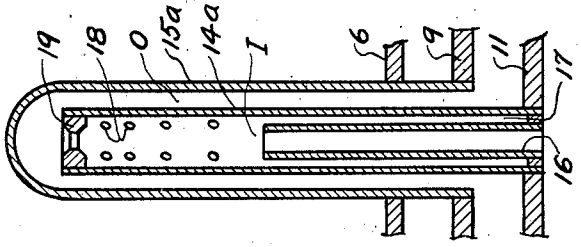


Fig-2

Fig-1

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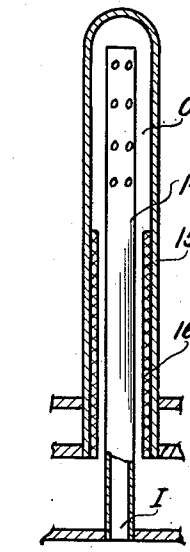


Fig-2a

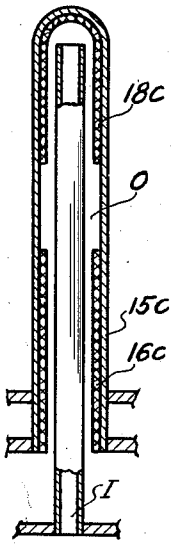


Fig-2b

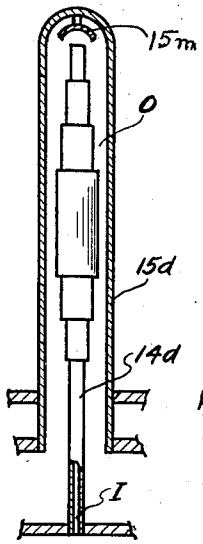


Fig-2c

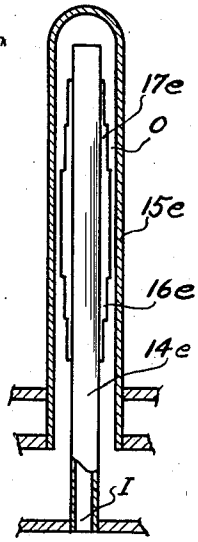


Fig-2d

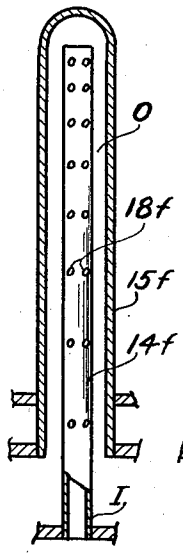


Fig-3

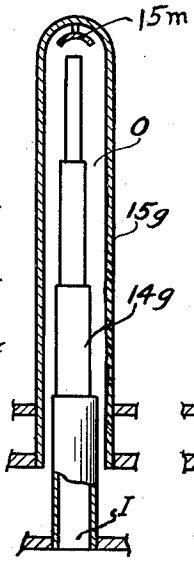


Fig-3a

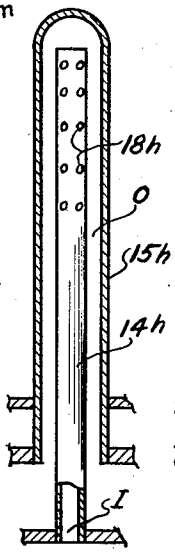


Fig-4

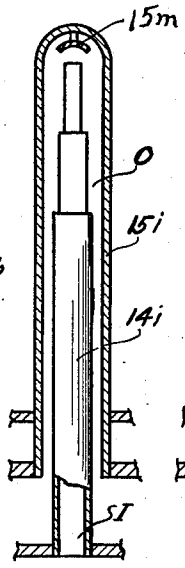


Fig-4a

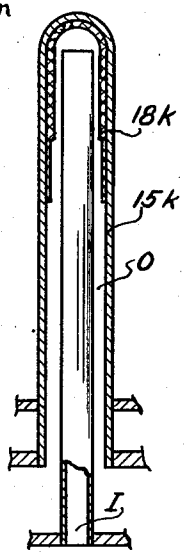


Fig-4b

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2,384,858

TEMPERATURE CONTROL OF CONTACTING REACTIONS

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Application December 6, 1941, Serial No. 421,916

3 Claims. (Cl. 252—242)

The present invention relates to contacting reactions and is concerned particularly with the use of contact material in a cycle of alternating reactions and to the efficient temperature control of such reactions.

The invention, although applicable to the treatment of various fluids, can well be exemplified by considering the on-stream treatment of high boiling hydrocarbons to obtain products having a lower boiling range, wherein during the on-stream treatment heat is used up by the reaction which must be supplied to the contact material in order to assist in and keep the reaction going. During this reaction period, the contact material, which is usually of a silicious nature, becomes contaminated with a carbonaceous deposit and after a predetermined length of time, the on-stream operation is stopped and the deposit removed. The nature of the deposit is such that it can be removed by burning or oxidation and consequently after the on-stream reaction is stopped, oxygen or oxygen containing gases are supplied to the zones of contact material in heated condition to effect the oxidation. During this oxidation period a large amount of heat is evolved and the temperature of the zones of contact material must be controlled by removing all or a portion of the evolved heat in order to prevent injury to the contact material or the converter structure. Prior practice has indicated that good temperature control is effected when imperforate tubes are interspersed within the zones of contact material to convey an extraneous fluid in indirect heat transferring relationship with the contact material.

In order to obtain the most effective temperature control of a body of contact material it is essential that provision be made for maintaining all portions of the body of material at the desired temperature and thus prevent undue acceleration or deceleration of a reaction as well as localized overheating or overcooling of the contact material. To this end the tubes should extend across the body of contact material in an equally spaced and uniform manner so that the zones of contact material between and around the tubes are at substantially the same temperature lengthwise of the tubes.

Various arrangements of imperforate tubes have heretofore been devised for controlling the temperature of and maintaining the contact material at the required temperature during the different reactions. In some instances heat exchange fluid has been circulated in one direction through a single tube in heat exchange relation with the contact material. In other cases U-shaped tubes have been used to circulate fluid in two directions through the contact material. Later developments, however, have shown that the most efficient temperature control is had when the heat exchange fluid is circulated in reverse flow through assemblages of nested tubes, each assemblage comprising an inner open end tube and an outer closed end tube positioned in spaced telescoping relation with each other so as to provide an outer chamber or annulus therebetween which is in communication with the inner passageway of the inner tube.

The assemblages of nested imperforate heat exchange tubes, described generally above, are quite satisfactory for proper temperature control with fluids which exist in liquid phase during at least a part of their use, such as fused salts, mercury or diphenyl and particularly when these fluids are supplied to the inner passageway and removed from outer annulus. Such fluids have a high heat capacity and therefore do not increase considerably in temperature during their passage through the outer tube or annulus. Consequently the temperature of the outer tube wall is reasonably constant in a lengthwise direction and the temperature of the contact material is thus maintained substantially constant.

It has been proposed to use steam or other gaseous or vaporous media, which are readily available to the industry, as an alternative means of close temperature control but because of the low heat capacity of this type of fluid it is necessary in order to transfer sufficient amounts of heat to supply the fluid at a relatively low temperature and remove it from the tube assembly at a much higher temperature. Due to this increase in temperature of the fluid in its passage through the tube assembly, the temperature of the fluid in the outer annulus varies lengthwise thereof to such an extent that the temperature of the outer tube wall and of the contact material controlled thereby is not proper for effective control.

In the contact treatment of hydrocarbons heretofore mentioned, the on-stream period preferably is operated in a manner to insure that the carbon is quite evenly deposited on the contact material so that during the regeneration period of the cycle substantially equal quantities of heat are evolved from equal zones of the contact material, and consequently the same amount of heat will be flowing all along the outer tube wall which must be removed uniformly in order to maintain the tube wall and contact material controlled thereby at the desired constant temperature.

However, because of the wide variation in the temperature when using a material of low heat capacity it is impossible to maintain the outer wall temperature of the ordinary nested heat exchange tube assemblage constant lengthwise thereof and consequently the temperature of the contact material surrounding the outer tubes varies substantially.

Our invention is concerned with a system of temperature control, which is particularly adapted for utilizing a gaseous heat exchange medium and to apparatus particularly adapted to function effectively in the system.

One object of the present invention is to provide method and apparatus for effective temperature control of contact masses by means of a gaseous or other low density heat exchange medium. Another object of the invention is to provide a temperature control system which provides for flexibility in the rate of heat transfer. Another object is to provide such a system which is economical and efficient in operation. Another object is to provide an efficient process for effecting a cycle of alternating contacting reactions. Another object of the invention is to provide heat exchange tube assemblages which permit efficient temperature control with a gaseous or vaporous heat exchange fluid. Other objects will become apparent from the detailed description which follows.

A better understanding of the invention will be had by reference to the accompanying drawings, in which

Fig. 1 generally is a diagrammatic representation, with some portions shown in detail, of one arrangement of apparatus which may be used for carrying out the present invention, and

Figs. 2, 2*a*, 2*b*, 2*c*, 2*d*, 3, 3*a*, 4, 4*a* and 4*b* are sectional views of reverse flow tube assemblages adapted for a gaseous or vaporous heat exchange medium.

Referring to Fig. 1 of the drawings, numerals 1, 2 and 3 represent a series of converters each of which provides a zone for contact material which is used to treat reactants during one period of a cycle of operation and which is then regenerated during the other period of the cycle of operation. Converter 3 only is sectioned to indicate its detailed structure but it is to be understood that converters 1 and 2, shown in elevation, are constructed similarly. In converter 3 is an upper transverse partition 4 secured in spaced relation with the converter end wall to provide an upper reactant manifold 5 and spaced a substantial distance from partition 4 is a lower transverse wall 6 forming a reaction chamber C for containing a body of contact material M. Partitions 4 and 6 are provided with apertures 7 and 8, respectively, which cooperate in the passage of fluid straight through the contact material or, if desired, sets of perforate conduits of the types shown in Patent 2,161,676 issued June 6, 1939, or Patent 2,163,599 issued June 27, 1939, to E. J. Houdry may be used to pass fluid in cross flow through the contact material. Secured below the transverse wall 6 is a tube sheet 9 forming therewith a lower reactant manifold 10 which cooperates with the upper manifold 5 in passing reactant fluid through the contact material M Heat exchange fluid manifolds are formed below the lower reactant manifold 10 by means of lower tube sheet 11 which is secured in spaced relation with upper tube sheet 9 and the lower end wall providing upper and lower heat exchange fluid manifolds 12 and 13, respectively. A plurality of reverse flow tube assemblages, generally indicated at A, comprising an open end inner tube 14 which is in communication with the lower heat exchange manifold 13, and closed end outer tube 15 which is in communication with the upper heat exchange manifold 12, are provided and extend across the body of contact material M in properly spaced and uniform relation so that the temperature of all portions of the body of contact material is controlled by these assemblages. The tubes are positioned in spaced relation with each other in order to provide an outer passageway which is in communication with the passageway of the inner tube so that the heat exchange fluid can be circulated from one heat exchange manifold to the other. For the purpose of differentiating in the relationship of the fluid in each passageway to the contact material, the fluid in the outer passageway or annulus will be considered as in "primary indirect" heat exchange relationship and the fluid in the inner passageway will be considered as in "secondary indirect" heat exchange relationship.

When it is desired to use a gaseous heat exchange medium to control the temperature of the above generally described converter, various factors, such as the amount of gaseous heat exchange medium available for use, the amount of heat to be extracted during a reaction and the volume of contact material to be controlled, must be taken into consideration. As heretofore mentioned, the temperature of a gaseous fluid will vary substantially between the inlet of the annulus and its outlet when using the ordinary reverse flow tube assemblages. Consequently, the temperature of the outer tube wall will vary accordingly and the temperature of the zone of contact material controlled thereby will vary greatly lengthwise of the tube. Generally speaking, these temperatures under varying conditions of operation, will follow three different temperature curves. For example, under a certain set of conditions the temperature will vary progressively upwardly from the inlet of the annulus to about the midpoint of the annulus and then vary progressively downwardly to the annulus outlet. Under certain other conditions of operation the temperature will vary progressively upwardly from the inlet of the annulus to the outlet and, depending on the amount of heat involved, the temperature may rise several hundred degrees from the inlet to the outlet. Under another set of operating conditions the temperature will vary progressively upwardly from the inlet of the annulus to a point midway of the annulus and then remain generally constant to the outlet. To further explain the temperature curves above mentioned, it may be stated generally that the first type of temperature curve will exist when the design of the ordinary reverse flow tube assemblages is such that the volume of the annulus or the outer passageway which is in primary indirect heat exchange relation with the contact material is substantially less than the volume of the inner tube or the passageway which is in secondary indirect heat exchange relation with the contact material. The second type of temperature curve will exist when the volume of the annulus is substantially greater than the volume of the inner tube, while the third type of temperature curve will exist when the volume of the annulus is approximately equal to the volume of the inner tube.

In Figs. 2, 2*a*, 2*b*, 2*c*, 2*d*, 3, 3*a*, 4, 4*a*, and 4*b* are sectional views of reverse flow heat exchange tube

assemblages which are adapted particularly for accurate temperature control when using a gaseous or vaporous heat exchange medium. These tube assemblages are designed to maintain the annulus temperature constant under varying conditions of operation. The assemblages of Figs. 2, 2a, 2b, 2c and 2d, for example, would be used when the temperature curve of the ordinary reverse flow tubes would be generally upwardly from the closed end of the outer tube or the inlet of the annulus to the midpoint of the annulus and then generally downwardly to the outlet of the annulus or open end of the outer tube. The assemblages of Figs. 3 and 3a would be used when the annulus temperature curve is generally upwardly from the inlet to the outlet. The assemblages of Figs. 4, 4a and 4b would be used when the temperature curve is generally upwardly to the midpoint of the annulus and constant to the outlet.

Referring to Fig. 2 the tube assemblage is constructed as indicated to provide an inner passageway I formed by the inner tube 14a and an outer passageway or annulus indicated at O, formed between inner tube 14a and outer tube 15a, which are in communication at the annulus inlet or upper end of the assemblage. The assemblage is constructed, as heretofore mentioned, to maintain the outer tube wall at a generally constant temperature lengthwise thereof and overcome the condition which would exist with the ordinary reverse flow tube assemblage, wherein the temperature curve would go up gradually from the inlet to the midpoint of the annulus and then go down gradually to its outlet. The assemblage may be considered as incorporated in the converters of Fig. 1, which will be assumed to be operated under conditions to give the temperature curve just mentioned when using the ordinary reverse flow tube assemblage with steam as the specific heat exchange medium.

A liner 16 is secured adjacent the lower end of the inner tube 14a and extends upwardly to about the midpoint of the tube to provide a space 17 which functions to decrease the temperature of the lower half of the outer tube wall and maintain it substantially constant by limiting the transfer of heat to the lower half of inner passage I to only that amount of heat which is transferred from the outer tube wall to the fluid in the lower half of annulus O. As the fluid in the passageway I moves upwardly it gradually becomes heated until its temperature is increased so greatly that at about the midpoint of the passageway its temperature difference with that of the fluid in the upper half of the annulus O is too small to transfer all heat reaching the outer tube wall to the fluid in the upper half of the inner passageway I, hence the temperature of the outer tube wall would tend to gradually rise from its upper or closed end toward its midpoint. The upper half of the inner tube 14a is modified to overcome this condition and to this end perforations 18 are provided therein, beginning at about its midpoint, which gradually increase in area toward the top of the tube and an orifice plate 19 is provided to decrease flow through the upper end and insure a gradually decreasing amount of steam flowing toward the upper end of the tube. This results in a temperature difference between the fluid in the upper half of annulus O and the upper portion of the outer tube wall which gradually increases from the midpoint toward the closed end of the outer tube wall and prevents a rise in temperature above that existing in its lower half which gives a substantially constant temperature all along the tube wall.

In Figs. 2a, 2b, 2c and 2d are shown alternative forms of tube assemblages which may be substituted for the assemblage of Fig. 2. In Fig. 2a the outer tube wall 15b is partially insulated at 16b to decrease the heat picked up by the fluid in the annulus O and thus raise the temperature of the tube wall in its lower half while the upper portion of inner tube 14b is perforated in a manner similar to Fig. 2 in order to maintain the upper half of the outer tube wall 15b at the same temperature at its lower half. Fig. 2b is similar to Fig. 2a in that the lower portion of outer tube 15c is insulated at 16c to increase the temperature of this portion of the tube wall while the upper portion of the outer tube is also insulated at 16c to raise the temperature in this portion and maintain it at substantially that of the lower portion. In Fig. 2c the inner tube 14d is constructed to increase the temperature difference in steps between outer tube wall 15d and steam in annulus O from its midsection toward both its upper and lower ends in order to raise the temperature at the ends and lower it toward the midsection. As shown, this is accomplished by constructing the inner tube in stepped portions which decrease in diameter from the midsection of the tube towards both ends. Fig. 2d is constructed to function in a manner similar to Fig. 2c and to this end stepped fins 16e and 17e are provided on inner tube 14e at its lower and upper ends, respectively.

Figs. 3 and 3a are constructed to maintain a constant temperature along the outer tube wall when the operating conditions are such that, with the ordinary reverse flow tube assemblage, the temperature of the outer tube wall would rise constantly from its closed end to its open end. In Fig. 3 perforations 18f are provided along the length of inner tube 14f and increase in area toward the closed end of outer tube 15f in order to gradually increase the temperature difference between the fluid in annulus O and outer tube wall 15f toward its closed end and thus increase the quantity of heat transferred from the closed end toward the open end of the outer tube 15f. In Fig. 3a, this is accomplished by constructing the inner tube 14g in stepped sections which decrease in diameter toward the closed end of the outer tube 15g.

Figs. 4, 4a and 4b are constructed to maintain a constant temperature along the outer tube wall when the operating conditions are such that, with the ordinary reverse flow tube assemblage, the temperature of the outer tube wall would rise from its closed end to about its midpoint and then remain substantially constant to its outlet. In Fig. 4 the inner tube 14h is provided at its upper end above its midpoint with perforations 18h which increase in area toward the closed end of outer tube 15h in order to progressively increase the temperature difference between the fluid in annulus O and tube wall 15h and progressively increase the quantity of heat transferred along the wall from about its midpoint to its closed end. In Fig. 4a this is accomplished by constructing the upper half of the tube 14i in stepped sections which decrease in diameter toward the closed end of the outer tube 15i. In Fig. 4b this is accomplished by providing insulation 18k at the closed end of outer tube 15k and gradually decreasing its thickness toward the midpoint of the tube.

The assemblages of Figs. 2c, 3a and 4a, as

shown, should be provided with baffles 15*m* adjacent the closed end of the outer tube in order to overcome the effect of the velocity of the vapors leaving the inner tube and thus prevent the formation of a cold spot.

Consider the invention as applied to the control of a particular hydrocarbon reaction, such as a cracking operation, wherein the original hydrocarbon charge is supplied in vapor phase to the contact material to effect the desired reaction and the alternate period of the cycle of operation or the period when the contact material is regenerated by effecting oxidation of any deposit. During the first mentioned or on-stream period the contact material is maintained above 800° F. to supply the heat necessary for the reaction and during the regeneration period the temperature of the contact material is controlled and kept below 1100° F. to prevent injury thereto and also to store some heat for the on-stream period of a succeeding cycle of operation. The heat exchange medium for example, steam, is circulated through the heat exchange system, during the regeneration period and in starting an operation the steam will be supplied from an outside source to line 21 where it is compressed in compressor 22 and sent to pipe manifold 23 at any desired pressure depending on its saturation point and at a temperature close to or above its saturation temperature. From the pipe manifold 23 the compressed steam will pass by lines 24, 25 or 26 to the lower heat exchange fluid manifold 13 of the converter or converters which are to be regenerated and then through the inner passageways I of the heat exchange tube assemblages where it will rise gradually in temperature and finally pass down through annulus O of the heat exchange tube assemblages to upper heat exchange fluid manifolds 12 and then passes out of the converter to the return pipe manifold 27 through lines 28, 29 or 30 at its increased temperature. The increase in temperature of the steam during its passage through the conduit assemblages is around 300° F. for this particular operation and the contact material will be kept at a temperature below 1100° F. during the entire regeneration period but at the end of this period or just prior to starting the succeeding on-stream period the temperature of the contact material will be around 875° F. and the heat stored in the contact material and converter structure will be sufficient to supply the necessary heat for the on-stream period so that the steam may remain quiescent.

From manifold pipe 27 the highly superheated steam is sent to a desuperheater indicated at 31 which may be a direct contact apparatus having a pump 32 for supplying water directly to the steam in the desuperheater through a temperature controlled valve 33 while condensate formed therein is removed through drain 34. The desuperheated steam vapors are drawn off through line 35 and their temperature may be raised to the desired degree by means of superheated vapors by-passed from pipe manifold 27 through valved line 36. Surplus steam formed in the desuperheater 31 can be withdrawn through the pressure regulated valve 37 in line 38 and the required steam for the heat exchange system returned to compressor 22 through line 21 and used in a subsequent regeneration.

In the desuperheating step of the above described operation water is required since it has the same chemical composition as the steam used in the heat exchange system. When other vapors or gases are used as the heat exchange medium it is to be understood that the superheated vapors leaving the heat exchange system will be desuperheated by a liquid having the same chemical composition as the particular vapor or gas used.

It is to be understood that various fluids other than steam may be used in carrying out the invention and that other tube construction can be used within the scope of the invention. It is to be further understood that heat exchange fins may be used in conjunction with the heat exchange tube assemblages when necessary to effect the desired temperature control. When reactant distributor and collector tubes, heretofore mentioned, are used in the converters shown in Fig. 1, it is also to be understood that the various tubes may be arranged in the converters in patterns designed to give the most efficient operation, for example, as shown in the copending allowed application of Eugene J. Houdry and Thomas B. Prickett, Serial No. 261,728, filed March 14, 1939, for Catalytic converter, now Patent No. 2,283,208.

We claim as our invention:

1. Method of removing heat from a zone of contact material wherein an exothermic regeneration reaction is being carried out which comprises circulating vapor through said zone in indirect heat exchange relation with the contact material at desired temperature and pressure to remove heat therefrom and to superheat the vapor, removing the superheated vapor from the reaction zone and desuperheating the same by contacting it with a liquid having substantially the same chemical composition, adjusting the temperature of the desuperheated vapor by adding superheated vapors thereto, removing excess vapor formed during the desuperheating step, compressing and returning the balance of the vapor at the desired temperature and pressure to the exothermic reaction zone and cyclically repeating the operation.

2. Method of removing heat from a zone of contact material wherein an exothermic regeneration reaction is being carried out which comprises circulating a vapor within said zone in indirect heat exchange relation with the contact material through inner and outer concentrically disposed channels at the desired temperature and pressure to remove heat from the contact material by superheating the vapor, removing the superheated vapor from the reaction zone and desuperheating the same by contacting it with a liquid having substantially the same chemical composition, adjusting the temperature of the desuperheated vapor by adding superheated vapors thereto, removing excess vapor which was formed during the desuperheating step, compressing and returning the balance of the vapor at the desired temperature and pressure to the exothermic reaction zone and cyclically repeating the operation.

3. Method of removing heat from a zone of contact material wherein an exothermic regeneration reaction is being carried out which comprises circulating a vapor within said zone in indirect heat exchange relation with the contact material through inner and outer concentrically disposed channels at the desired temperature and pressure to remove heat from the contact material by superheating the vapor, varying the velocity of the vapor between the inlet and outlet of the outer channel so as to maintain the temperature of the contact material substantially

constant lengthwise of the outer channel, removing the superheated vapor from the reaction zone and desuperheating the same by contacting it with a liquid having substantially the same chemical composition, adjusting the temperature of the desuperheated vapor by adding superheated vapors thereto, removing excess vapor which was formed during the desuperheating step, compressing and returning the balance of the vapor at the desired temperature and pressure to the exothermic reaction zone and cyclically repeating the operation.

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