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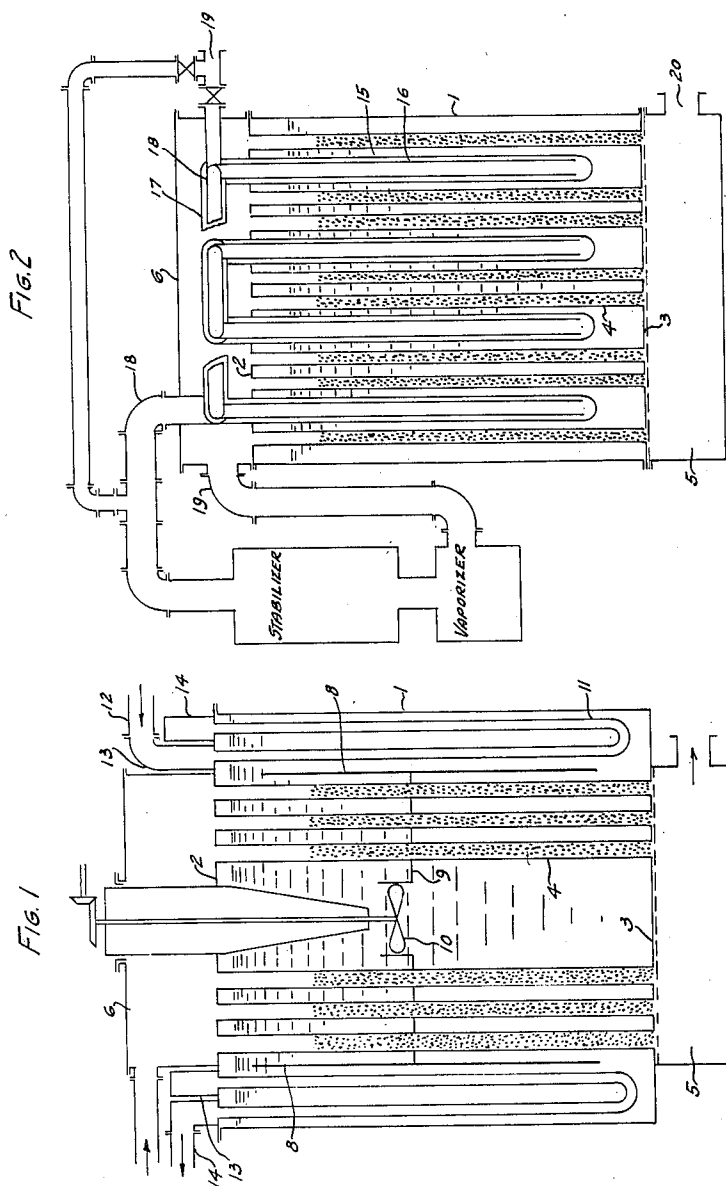
A. O. JAEGER

1,945,812

CATALYTIC APPARATUS

Filed July 1, 1931

2 Sheets-Sheet 1



INVENTOR

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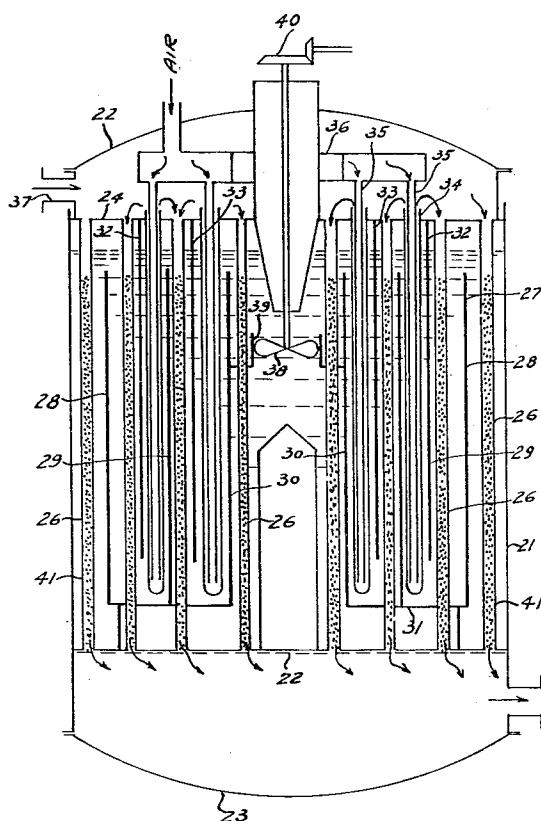
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CATALYTIC APPARATUS

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2 Sheets-Sheet 2

FIG. 3



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1,945,812

CATALYTIC APPARATUS

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Application July 1, 1931. Serial No. 548,084

8 Claims. (Cl. 23—288)

This invention relates to apparatus for effecting catalytic reactions, and more particularly to apparatus for such purposes in which a temperature gradient is maintained throughout the length of the catalyst mass.

In the past exothermic vapor phase reactions have been carried out in converters cooled by means of various baths, both boiling and non-boiling. Baths which boil at or below the reaction temperature are useful because they act as a thermostat and prevent undue rises in catalyst temperature, but when high yields are desired it is impossible to maintain any appreciable difference in temperature between the first and last portions of the catalyst and consequently a considerable portion of the reaction goes beyond the desired product, since many of the reaction products are extremely sensitive to high temperatures. For this reason non-boiling baths have been developed in which the exotherm of the reaction is conducted away as sensible heat, thus permitting the latter parts of the catalyst to be maintained at suitably lower temperatures in order to prevent the reaction from going too far in these zones.

The most efficient converters of this type have been those in which vertical catalyst tubes are used, since the natural thermosiphon flow of the bath liquid tends to retain higher temperatures at the top than at the bottom and the more rapid reaction taking place when the fresh gases first strike the catalyst is controlled by bath liquid of suitably higher temperatures. In many installations this natural thermosiphon flow has been directed and enhanced by suitable baffle systems and impelling means as described in my prior application Serial No. 425,831 filed February 4, 1931, the bath liquid passing through zones containing catalyst tubes and then through cooling zones in which the heat taken up is removed by heat exchange with cooling media. Such cooling devices as tubes containing boiling liquids or heat exchangers through which gases or liquids are passed have been used for this purpose.

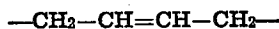
According to the present invention gaseous cooling media are used for removing the reaction heat taken up by the boiling bath, and the heat exchange elements are arranged in such a manner that the natural thermosiphon flow of the bath liquid, is exercised to its fullest extent while at the same time a very efficient heat exchange takes place. To accomplish this object, vertical heat exchange elements are provided in the bath liquid, either interspersed among the catalyst tubes when an accurately defined path

of the bath liquid is not desired or immersed in the cooling zones when such zones are used. The vertical travel, both of the bath liquid and of the cooling gases insured a most efficient form of heat exchange while at the same time the desired difference in temperature between the upper and lower portions of the bath liquid is maintained.

In the accompanying drawings three representative converter types are illustrated in which the principles of the present invention are applied, but it is to be understood that the invention is not limited to converters of these types. On the contrary, vertical heat exchange elements may be employed to advantage with non-boiling bath converters of any desired type, and all such installations are included within the scope of the invention.

While the present invention is applicable to all exothermic catalytic vapor phase reactions it is particularly suitable for the catalytic oxidation of organic compounds or for the purification of organic compounds by catalytic combustion of impurities. A few typical examples are as follows:

1. Reactions in which an intermediate oxidation product is produced. The oxidation of benzol, toluol, phenol, tar phenols or furfural and other compounds containing the group



to maleic acid and fumaric acid or mesotartaric acid; cresol to salicylaldehyde and salicylic acid; toluol and the various halogen and nitro substituted toluols to the corresponding aldehydes and acids; xylenes, pseudocumene, mesitylene, paracymene and other derivatives to the corresponding aldehydes and acids; naphthalene to naphththaquinone, phthalic anhydride and maleic acid; phthalic anhydride to maleic acid and fumaric acid; anthracene to anthraquinone; phenanthrene to phenanthraquinone, diphenic acid, phthalic anhydride and maleic acid; acenaphthene to acenaphthylene, acenaphthaquinone, bisacenaphthylidenedione, naphthaldehydic acid, naphthalic anhydride and hemimellitic acid; fluorene to fluorenone; eugenol and isoeugenol to vanillic acid; methyl alcohol and methane to formaldehyde; ethyl alcohol to acetic acid; ethylene chlorhydrine to chloracetic acid and the like.

2. Reactions in which an undesired impurity is burned out, such as the purification of crude anthracenes of various degrees of impurity with total combustion of carbazole, dead oils and in some cases phenanthrene; purification of crude

naphthalenes and crude mononuclear hydrocarbons, such as benzols and the like; purification of ammonia from coal tar with the burning out of the organic impurities such as phenolic bodies present, etc.

3. Oxidation of mixtures of organic compounds to desired intermediate products with removal of impurities such as the oxidation of crude anthracenes, phenanthrenes, and the like to intermediate products such as anthraquinone, phenanthraquinone, diphenic acid, phthalic anhydride, and the like with concomitant removal of carbazole and dead oils by total combustion; the oxidation of crude tar acids to maleic and fumaric acids with the combustion of certain impurities, etc.

Certain reductions such as the reduction of nitro compounds to amines or hydrogenated amines as, for example, the catalytic reduction of nitrobenzene, dinitrobenzene, nitrophenol, nitronaphthalene, etc. can be carried out using the principles of the present invention. Of course in such cases hydrogen or the necessary hydrogen-containing mixtures will be used instead of air or oxygen-containing gases which are employed in the organic oxidations. The reduction of oxides of carbon to methanol, methane, higher alcohols and ketones or petroleum-like products; the hydrogenation of aromatic compounds to alicyclic compounds such as, for example, benzene to cyclohexane, naphthalene to tetraline or decaline, anthracene to hydrogenated anthracenes, phenol to cyclohexanol form another class. The reduction of unsaturated aliphatic hydrocarbons such as acetylene to ethylene or ethane and the like are also of importance and require a very careful temperature control. It should be noted that in the case of reactions, such as the reduction of oxides of carbon to acetylene, vaporization of the components is not necessary and the heated gases serve, therefore, to preheat the mixture to the desired temperature. While these reactions utilize the heat of the bath effectively they do not utilize it both for preheating and for supplying the latent heat of vaporization as in the case of materials which have to be vaporized.

A number of complex reactions such as combined reduction and splitting, as, for example, the transformation of pyridine to amyl amine come within the purview of the present invention, as do complex reductions. Thus, for example, oxides of carbon may be reduced in the presence of the vapors of many organic compounds. For example, they may be reduced in the presence of aliphatic hydrocarbons, such as paraffins, olefines, acetylenes, hydrocarbons having the formula C_nH_{2n-4} , C_nH_{2n-6} , etc. Hydrogen may be present or absent, and the class of products obtained, such as mixtures of oxygenated compounds, or in many cases oils which are predominately hydrocarbon in their nature, will vary with the amount of reacting ingredients and with the contact masses and reaction conditions used, and it is an advantage of the present invention that these novel combined reductions can be carried out in the desired direction with great effectiveness by the incorporation of suitable stabilizer promoters or stabilizers in the contact masses.

Another class of combined reaction consists in the reduction of oxides of carbon with or without hydrogen in the presence of vapors of aliphatic alcohols, such as paraffin alcohols having the formula $C_nH_{2n+1}OH$, or unsaturated

alcohols having the formula $C_nH_{2n-1}OH$, or $C_nH_{2n-3}OH$, etc. Polyvalent alcohols such as glycol, glycerol and the like, may be reduced in combination with oxides of carbon with or without hydrogen.

Oxidation products of alcohols, such as for example, saturated or unsaturated aldehydes and ketones, or oxidation products of polyvalent alcohols, such as glycol-aldehydes, glyoxal, glyoxylic acid, oxalic acid, and the like, may be used for vapor phase reductions in the presence of oxides of carbon and hydrogen. Oxidation products of trivalent alcohols and divalent isomeric alcohols may also be used, of course only where it is possible to obtain the vapors of the compounds without undesired decomposition.

Aliphatic acids form another important class of compounds which can be reduced in combination with oxides of carbon. The acids include fatty acids, oxyacids, lactones, polybasic acids, ketone acids, and the like. Other miscellaneous aliphatic carbonyl compounds such as aldehyde alcohols, diketones, triketones, oxymethylene ketones, ketone aldehydes, ketone alcohols and the like, may also be combined with oxides of carbon and reduced in the presence of the contact mass described above to form many valuable products.

In addition to compounds of the aliphatic series which may be reduced together with oxides of carbon, various compounds of the alicyclic series, such as for example, alicyclic compounds, for instance, cycloparaffins, cycloolefines, cycloolefines may be combined with oxides of carbon and reduced. Examples of specific members of this class are cyclohexane, cyclopentadiene, dicyclopentadiene, and the like. Of course alicyclic carbonyl compounds, such as cyclohexanol, cyclohexanone, etc., may be used, it being understood in this connection and throughout the specification that any compound containing to CO group, irrespective of whether the oxygen is united to carbon with a single or a double bond, are included under the term carbonyl compounds.

Aromatic compounds, such as benzene hydrocarbons, naphthalenes, anthracenes, phenanthrenes, phenols, aromatic alcohols, aldehydes, ketones and acids may be reduced in the presence of oxides of carbon and hydrogen, of course only insofar as the products are capable of volatilization without undesired decomposition.

Heterocyclic compounds, such as products containing the furane nucleus, pyrrole bodies, pyrrolidines and the like, may be reduced together with oxides of carbon.

In the inorganic field the synthesis of ammonia can be effectively carried out, all of the heat being conserved in a very efficient manner by passing the nitrogenhydrogen mixture or part of it as the cooling agent for the bath.

In the drawings:

Fig. 1 is a vertical section through a simple type of converter using a positively recirculated bath in which the cooling is effected in a zone remote from that of the catalyst tubes;

Fig. 2 is a vertical section through a converter with vertical heat exchange elements distributed among the tubes; and

Fig. 3 is a vertical section through a converter designed for extremely close control of reaction conditions in which a plurality of catalyst zones and a plurality of cooling zones are provided, the bath passing successively through alternate zones.

The converter shown in Fig. 1 consists of a converter shell 1, a bottom tube sheet 3 rigidly fastened to the converter shell, and tubes 4 extending upwardly from the bottom tube sheet and supporting an upper tube sheet 2. The bottom piece 5 serves as an exhaust gas collector and a top piece 6 serves as a reaction gas inlet, the reaction gases passing downwardly through the tubes 4 which may be completely or partly filled with catalyst. A cylindrical vertical baffle 8 is provided surrounding the bundle of tubes and defining with the converter shell a cooling chamber external to the catalyst tube zone.

The converter is filled with a non-boiling bath to a point above the top of the vertical baffle 8 as indicated on the drawing, and a horizontal baffle 9 and impeller 10 are provided to bring about a positive circulation of the bath liquid upwardly from the tubes and then down between the vertical baffle 8 and the converter shell 1. In this cooling chamber are placed U tubes 11 through which the cooling gas circulates from the intake pipe 12 and passes through the exit pipe 14 which is arranged as a manifold above the exit side of the U tubes 11. Similarly, the intake pipe 12 is manifolded as shown at 13, so that the passage of the cooling gas through the U tubes is downwardly through the inner leg and upwardly through the outer leg. By this provision the cold incoming gases pass first in heat exchanging relation with the hot liquid flowing over the top of the baffle 8 and pass in cocurrent therewith through the entire length of the cooling zone, thus providing an intimate heat exchange. Since a cocurrent flow will not raise the temperature of a cooling gas to the temperature of a liquid to be cooled, the gases passing upwardly through the outer leg of the U tube 11 are still below the temperature of the bath flowing over the top of the baffle 8 and are therefore capable of extracting more heat during their upward passage.

For convenience the operation of the converter will be described in connection with the oxidation of naphthalene to phthalic anhydride, it being understood of course that it is generally suitable for other exothermic reactions described above. In operation, therefore, the converter is filled with suitable bath, for example a molten eutectic mixture of sodium nitrate and sodium nitrite which is heated to about 400° C. by any suitable means, for example by passing hot gases through the catalyst tubes from a gas preheater. As soon as the bath is at the desired temperature a vaporous naphthalene-air mixture, for example in the ratio of 1 gram of naphthalene to 18 liters of air, is passed through the catalyst tubes 4, being oxidized to phthalic and generating heat which is absorbed by the bath. At the same time, a cooling gas such as air is admitted through the pipe 12 and passes through the U tubes 11, taking up heat from the bath liquid in the cooling zone. The natural thermosiphon flow of the bath liquid over the top of the baffle 8, which is enhanced by the action of the impeller 10, keeps a continuous flow of heated bath through the cooling zone and consequently a very satisfactory temperature control is maintained throughout the converter.

With reactions where the heat evolution is not excessive and a positively defined circulation of bath liquid is not necessary, the construction of the converter is somewhat simplified by interspersing heat exchange elements among the catalyst tubes. Such a construction is illustrated in Fig. 2, which also shows the use of pre-

heated cooling air for vaporizing the reaction mixture as is more specifically claimed in my prior application Serial No. 448,410, filed April 29, 1930. The construction of Fig. 2 is well suited for the oxidation of toluene to benzaldehyde and benzoic acid or of anthracene to anthraquinone. This converter is similar to that of Fig. 1 in that it consists of a shell 1, bottom and top pieces 5 and 6, upper and lower tube sheets 2 and 3 and catalyst tubes 4, but heat exchange elements of a different type are preferably employed. These heat exchange elements consist of telescoping outer and inner tubes 15 and 16, the outer tubes being closed at their lower ends and both sets of tubes being headed into upper manifolds 17 and 18 as shown. The incoming cooling gases enter the inner manifold 18 through the pipe 19, pass downwardly through the inner heat exchange tubes 16 and upwardly through the outer tubes 15, being collected in the outer manifold 17 and led through the pipe 18 into a stabilizer for suitably adjusting their temperature and then into a vaporizer, where they are used for vaporizing the toluene or other substance to be vaporized and reacted. Gases from the vaporizer enter the converter at 19 and pass downwardly through the catalyst tubes 4, the product leaving the converter at 20.

Since the sensitive but not excessively exothermic reactions of this type take place quite rapidly the greater amount of reaction occurs in the upper portions of the catalyst tubes, the added length being useful to obtain high purity or yields of the reaction product. In order to prevent overcooling of the catalyst and at the same time to cool the lower portion of the converter sufficiently to prevent destruction of benzaldehyde and benzoic acid in the presence of the oxidation catalyst, the incoming cooling gases are first passed into direct heat exchanging relation with the bath liquid at the lower portions of the outer tubes 15. This zone, where the coldest gases first come into direct heat exchanging relation with the bath, is thus subjected to powerful cooling which prevents excessive oxidation of the reaction product, while continued absorption of heat as the gases rise in the outer tubes 15 prevents overcooling of the bath liquid surrounding the upper portions of the catalyst tubes.

The converter shown in Fig. 3 is one in which a close control of the flow of bath liquid is maintained throughout its entire travel, thus maintaining an accurately regulated temperature gradient throughout the entire length of the catalyst tubes and insuring maximum outputs and yields of the reaction product. Such converters are well suited for reactions in which a very close control of reaction temperature is desirable and are particularly suited for the oxidation of anthracene to anthraquinone. The converter consists of an outer shell 21, top and bottom pieces 22 and 23, upper and lower tube sheets 24 and 25 and catalyst tubes 26. Groups of these catalyst tubes are arranged in zones, each group being illustrated on the drawings by a single catalyst tube, and it should be understood that in installations of commercial size several hundred of these tubes are included in each group. The number of tubes and the relative grouping of the tubes depends to a certain extent upon the size and shape of the converter; in larger installations circular or hexagonal converters are used so that the groups of tubes may be equally spaced from each other. In the construction shown four such groups are illustrated,

each group being separated from the next by baffles defining a cooling zone, in which vertical heat exchange elements for the passage of a cooling gas are suspended. The specific baffle system shown comprises a lower baffle structure 27, consisting of outer, intermediate and inner baffles 28, 29 and 30 which are joined by the annular horizontal baffle 31. Upper baffles 32 and 33 are suspended between lower baffles 28, 29 and 29, 30 respectively in order to divide each of the spaces between said lower baffles into a reaction zone containing catalyst tubes and a cooling zone containing vertical heat exchange elements. Heat exchangers of any approved type may be used, those shown in the drawing being similar to the heat exchangers of Fig. 2 and consisting of outer closed end tubes 34 and inner open end tubes 35 joined at their upper ends by manifold 36 through which air or other cooling gas is introduced. The outer tubes 34 are shown as being open at their upper ends, which project slightly above the upper tube sheet 24 in order to more effectively mix the gases leaving the heat exchangers with anthracene or other reaction vapors entering the converter at 37. This type of heat exchange element design can only be used in reactions such as the oxidation of anthracene to anthraquinone or toluene to benzaldehyde and benzoic acid where the amount of cooling air required does not exceed the volume of air present in the reaction mixture. The design is not suitable for the oxidation of naphthalene to phthalic anhydride where the amount of air for cooling is far in excess of that required in the reaction mixture but if a manifolding system is used as in Figs. 1 and 2 converters with multiple reaction zones can be very effectively utilized in the production of phthalic anhydride.

In the operation of this converter the anthracene or other material to be reacted is vaporized with steam or other non-oxidizing gases and admitted to the upper portion of the converter while the cooling air enters the upper manifold 36 as shown, passes through the heat exchange elements in the cooling zones and is then admixed with the vaporized anthracene to form a reaction mixture suitable for oxidation by the catalyst in the reaction zones to anthraquinone. The mixture of air with the vaporized anthracene immediately prior to introduction into the catalyst obviates the dangers of explosions in the vaporizer and pipes, which is a serious problem with anthracene owing to the presence of pyrophoric impurities. The heat given off by the reaction is conducted away by a non-boiling bath of lead or sodium nitrate-sodium nitrite, which is filled into the bath space provided by the outer shell 21 and lower tube sheet 22 to a level above the tops of the lower baffle structure 27. Recirculation of this bath is insured by the impeller 38 operating in a central well 39 and actuated by suitable gears 40, thus permitting the speed of recirculation to be altered in accordance with changing conditions in the operation. The bath liquid travels upwardly along the catalyst tubes in each of the reaction zones and downwardly along the cooling tubes in each of the cooling zones, where it passes counter-current to a rising stream of air in the outer tubes 34. By reason of the positive cooling attained in each of these zones the temperature of the bath is considerably lower throughout the lower portions of the converter than in the upper portion, and consequently an effective and

closely controlled temperature gradient is maintained throughout the catalyst. The bath liquid passing over the outer baffle 28 is not subjected to positive cooling but is passed downwardly along the outer catalyst tubes 41 and under the horizontal baffle 31 into the central well space. The outer tubes 41, which would otherwise be uniformly cooled throughout their length by radiation from the converter shell, are therefore heated at their upper portions by the hot liquid flowing over the outer baffle 28 and thus a temperature gradient is maintained in these tubes also.

The above converters have been described in connection with reactions in which the highest catalyst temperatures are preferably maintained in the zones where the fresh reaction gases are admitted. Should it be desired to maintain the highest temperatures in the latter portions of the catalyst, as may be done in such processes as the selective combustion of organic impurities referred to, it will be obvious that the operation of the converters can readily be reversed, the reaction gases passing in at the bottom and out at the top, with or without reversal of the flow of cooling gases through the heat exchangers. Similarly, for endothermic or only slightly exothermic reactions heating instead of cooling gases may be used in the heat exchangers without departure from the principles of the invention.

It will thus be seen that the combination of vertical heat exchange elements with vertical catalyst tubes, operating in a non-boiling bath which conducts away the exotherm of the reaction as sensible heat, a uniform and highly desirable temperature gradient is readily maintained in converters of the most varied types, thus maintaining the most desirable reaction conditions in converters which do not have to withstand the high pressures necessary when boiling baths are used. While the invention has been described in connection with exothermic organic oxidations, it is understood that the same principles will apply when other exothermic reactions such as reductions and hydrogenations are effected, in which case hydrogen or other reducing agents may be used as the cooling agent if desired. This application is a continuation in part of my prior application, Serial No. 448,410, filed April 29, 1930, now Patent 1,850,797.

What is claimed as new is:

1. Apparatus for carrying out exothermic catalytic vapor phase reactions comprising in combination a converter containing vertical catalyst tubes, a bath liquid surrounding said tubes and in direct heat exchange relation therewith and having a boiling point above the temperature of the reaction to be carried out, and vertical heat exchange elements adapted for the passage of a gaseous cooling medium immersed in said bath liquid.

2. Apparatus for carrying out exothermic catalytic vapor phase reactions comprising in combination a converter containing vertical catalyst tubes, a bath liquid surrounding said tubes and having a boiling point above the temperature of the reaction to be carried out, a vertical baffle surrounding said tubes and extending from a point above the bottom of the bath compartment to a point below the upper surface of the bath and being spaced from the converter shell sufficiently to define therewith a cooling chamber, and vertical heat exchange elements adapted for passage of a gaseous cooling medium immersed in said bath liquid in said cooling chamber.

3. Apparatus for carrying out exothermic catalytic vapor phase reactions comprising in combination a converter containing vertical catalyst tubes, a bath liquid surrounding said tubes and in direct heat exchange relation therewith and having a boiling point above the temperature of the reaction to be carried out, and vertical heat exchange elements comprising open end inner tubes surrounded by closed end outer tubes immersed in said bath liquid.

4. Apparatus for carrying out exothermic catalytic vapor phase reactions, comprising in combination a converter shell, a lower tube sheet retained across said converter shell and cooperating therewith to produce a bath space, vertical catalyst tubes secured in said lower tube sheet, a bath liquid surrounding said catalyst tubes and in direct heat exchange relation therewith and having a boiling point above the temperature of the reaction to be carried out, a manifold for the introduction of a cooling gas in the portion of the converter above said bath space, and vertical heat exchange elements attached to said intake manifold and extending into said bath liquid substantially parallel to said catalyst tubes.

5. Apparatus for carrying out exothermic catalytic vapor phase reactions, comprising in combination a converter shell, a lower tube sheet retained across said converter shell and cooperating therewith to produce a bath space, vertical catalyst tubes secured in said lower tube sheet and extending through an upper tube sheet, a bath liquid surrounding said catalyst tubes and in direct heat exchange relation therewith and having a boiling point above the temperature of the reaction to be carried out, a manifold for the introduction of a cooling gas in the portion of the converter above said upper tube sheet, and vertical heat exchange elements attached to said manifold and extending into said bath liquid substantially parallel to said catalyst tubes, said vertical heat exchange elements consisting of inner open end tubes attached to said intake manifold at their upper ends surrounded by outer tubes closed at their lower ends.

6. Apparatus for carrying out exothermic catalytic vapor phase reactions, comprising in combination

a converter shell, a lower tube sheet retained across said converter shell and forming therewith a bath space, vertical catalyst tubes extending upwardly from said lower tube sheet, a bath liquid surrounding said catalyst tubes and in direct heat exchange relation therewith, at least one vertical baffle surrounding at least a portion of said catalyst tubes to provide a reaction zone and a cooling zone, and vertical heat exchange elements adapted for the passage of a gaseous cooling medium extending into the bath liquid in said cooling zone.

7. Apparatus for carrying out exothermic catalytic vapor phase reactions comprising in combination a vertical shell, a lower tube sheet attached to said converter shell and forming therewith a bath space, vertical catalyst tubes extending upwardly from said lower tube sheet, a bath liquid having a boiling point above the temperature of the reaction to be carried out surrounding said catalyst tubes and in direct heat exchange relation therewith, heat exchange elements adapted for the passage of a gaseous cooling medium interspersed among said vertical catalyst tubes and extending into the bath liquid, and means for passing a cooling gas through said heat exchange elements.

8. An apparatus for carrying out exothermic catalytic vapor phase reactions comprising in combination a vertical shell, a lower tube sheet attached to said converter shell and forming therewith a bath space, groups of vertical catalyst tubes attached to said lower tube sheet and extending upwardly to an upper tube sheet, a bath liquid having a boiling point above the temperature of the reaction to be carried out surrounding said catalyst tubes, lower vertical baffles submerged in said bath liquid between groups of catalyst tubes, upper vertical baffles extending above the level of the bath liquid interspersed between said lower vertical baffles and said groups of catalyst tubes, and vertical heat exchange elements adapted for the passage of a cooling gas extending into said bath liquid in the spaces between upper and lower vertical baffles.

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