

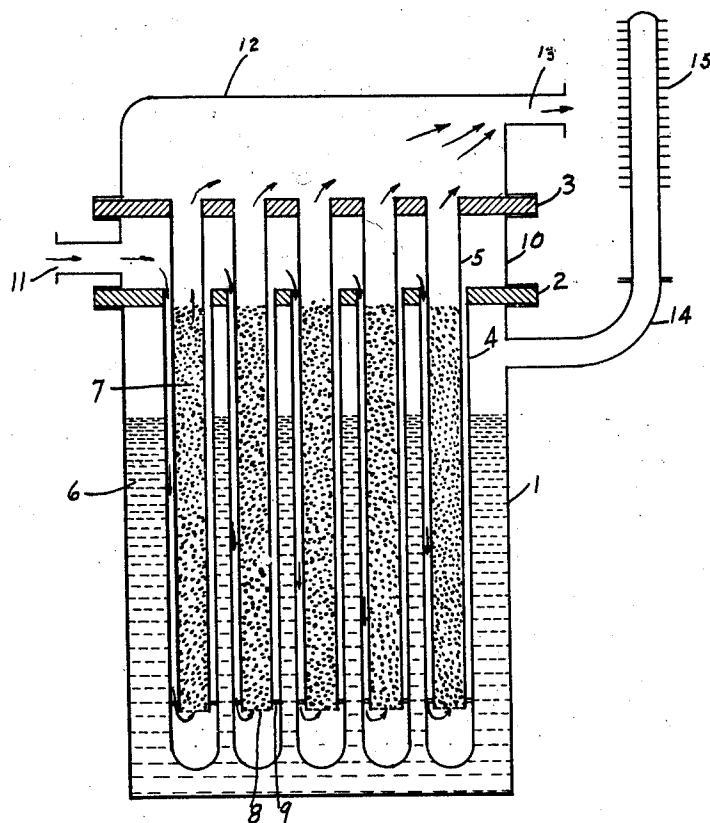
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CATALYTIC APPARATUS AND PROCESS

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CATALYTIC APPARATUS AND PROCESS

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This invention relates to processes of carrying out exothermic catalytic reactions, and more particularly to vapor phase catalytic reactions involving the transformation of carbon or nitrogen containing compounds in which the temperature regulation is effected by a boiling bath.

Liquid cooled converters, especially those cooled by utilizing a boiling bath, have found considerable use in the art of vapor phase catalysis as the temperature control is extraordinarily powerful and uniform. The ordinary type of liquid cooled converter is built in the form of a fire tube boiler, with the catalyst in the flues. This construction permits a very satisfactory temperature regulation, but possesses several disadvantages. In the first place all of the catalyst is normally in direct heat exchanging relation with the bath liquid, and, especially where the latter boils, a very powerful temperature regulation takes place which is uniform throughout the mass of the bath. For many catalytic reactions this uniformity is desirable but for others it is desirable to have a temperature gradient through the catalyst so that some portions may be at a higher temperature than others. This is particularly true of equilibrium reactions, where the temperature for maximum reaction velocity is much higher than that for maximum conversion yield. It is also desirable in many reactions to rapidly cool off the products after they have reacted in order to prevent decomposition of the reaction product. This cannot be practically effected in a bath cooled converter, especially of the boiling bath type, for unless all of the contact mass is in heat exchanging relation with the bath no accurate control is obtained, and if all of the contact mass is in heat exchanging relation with the bath it is not possible to cool off a portion of the contact mass rapidly to a relatively lower temperature.

Another disadvantage of the ordinary fire tube boiler type of bath converter lies in the fact that a large number of joints are required to be liquid and vapor tight, and as many catalytic reactions take place at high temperatures, in the neighborhood of 400° C., and as many of the bath liquids, especially boiling baths, consist of metals or metal alloys of very high specific gravity, such as mercury or mercury alloys, the converter is subject to serious strains, both due to the high temperatures and to the great weight of bath.

In the ordinary type of converter preheating of reaction gases is normally effected by filling the catalyst tubes only partly full of contact mass and utilizing the upper, empty portions of the

tubes as preheaters, they being kept in contact with the vapors of the bath, where the latter boils, or with the bath itself in the case of a non-boiling bath. This construction operates satisfactorily for many purposes, but requires a fairly long length of preheating tube as the size of the tube must be fairly large in order to provide sufficient contact space, and the heat transfer is not as good as with very small gas passages.

The necessity of providing for adequate preheating also requires longer tubes than would otherwise be necessary, which considerably increases the weight and size of the converter.

The converters of the present invention possess most of the advantages of ordinary bath cooled converters and in addition avoid a number of the disadvantages. In the first place the number of vapor tight joints is cut in two, and in the preferred embodiment, the joints do not have to bear any weight of bath liquid. Adequate preheating of the incoming gases is provided without any additional tube length, and parts of the contact mass are cooled by the bath while other parts are cooled by incoming reaction gases, permitting the maintenance of a temperature gradient in the contact mass. If the ordinary converter may be considered as a modified fire tube boiler the converter of the present invention might be considered as a modified Field tube boiler. Instead of tubes passing completely through the liquid and requiring joints in an upper and lower tube sheet, closed end tubes extend from a single tube sheet and the other end of the converter is solidly closed. A second set of open end tubes extend concentrically into the closed end tubes, leaving an annular space between the two. The catalyst is placed in the open end tubes and reaction gases are preheated by passing through the annular space between the catalyst tube and the closed end tubes. Thus the catalyst temperature is modified, not only by the bath but by the incoming reaction gases, and a portion of the catalyst may have its temperature controlled entirely or primarily by the reaction gases. At the same time the annular space is preferably chosen so that the portion of the contact mass below the bath level transfers its heat readily to the bath, and an accurate temperature control is made possible.

The invention will be described in greater detail in connection with the drawing, which shows a vertical section through a typical converter embodying the principles of the present invention. The drawing is purely diagrammatical, and represents one simple modification.

The converter consists of a shell, or tank, 1, closed at its top with a tube sheet 2, from which closed end tubes depend. A second shell ring 10, above tube sheet 2, supports a second tube sheet 3, and forms with the tube sheets a gas inlet chamber. Open end tubes 5 depend from the tube sheet 3, extending concentrically into the tubes 4 and being spaced therein by the spacer 9. At the bottom of the tubes screens 8 are provided which retain the catalyst 7, shown conventionally by stippling. The latter, in the preferred embodiments, extends above the level of the bath 6, but if desired, of course, may not extend as high. A gas inlet 11 is provided in the inlet chamber and a top piece 12 fits over the tube sheet 3, being provided with an outlet pipe 13. If the bath 6 is to boil the vapors pass out through the pipe 14 into a reflux condenser 15, shown conventionally as an air cooled reflux of the steam superheater type. The drawing is purely diagrammatical and in practice, of course, the converter will be provided with the usual accessories, such as lagging, heating means, if necessary, temperature measuring devices, and the like. As the particular design of these accessories forms no part of the present invention they have been omitted for the sake of clearness, and the chemical engineer will choose a suitable type.

In operation the bath 6 is brought up to the desired temperature and may, for example, boil, thus continually being maintained at a predetermined temperature. The boiling may be at atmospheric pressure or at a pressure above or below the atmosphere, suitable pressure regulating means being applied to the reflux 15, as is well known in the art. Where boiling metal baths are used it is normally desirable to provide an atmosphere of inert gases above them. When the bath has reached the required temperature the reaction gases are passed in through pipe 11, and flow down through the annular space between the tubes 4 and 5. It will be noticed that the incoming gases are preheated by the vapors of the bath through the walls of the tubes 4, and also by the portion of the contact mass above the level of the liquid. This portion of the contact mass, therefore, has its temperature regulated primarily by the reaction gases, and may be at a temperature very materially below that of the boiling bath, a marked advantage of the present invention. The gases are then rapidly heated up, both by the contact mass and by the bath itself, and the heating is a very efficient one since the annular space can be made very small with correspondingly high gas speeds and extremely efficient heat transfer. After reaching the bottom of the closed end tubes the gases reverse their flow, as shown by the arrows, and pass upwardly through the contact mass, the reaction taking place and any heat given off, in the case of exothermic reaction, being used both for preheating the incoming gases and for causing the bath to boil. The reaction being most intense in the portion of the contact mass where it encounters the fresh reaction gases, the greatest heat will be evolved there in the case of an exothermic reaction. This will result in a very vigorous circulation, boiling and geyser action of the bath, which is most desirable for efficient temperature regulation and is considerably more effective than the ordinary fire tube type of converter where normally the reaction gases pass downwardly through the catalyst tubes. In such a converter, unless

care is taken, the reaction may take place practically entirely in the first few inches of contact mass, which will result in the upper part of the bath boiling whereas the lower part may be at a much lower temperature, and what is worse at a temperature which cannot be accurately controlled.

It will be noted that the only joints which have to be both gas tight and vapor tight are those between the closed end tubes 4 and the tube sheet 2. As the tube sheet 2 has only to sustain the relatively slight weight of the thin tubes 4 no great mechanical strain is placed on the joints, which greatly simplifies their production and which assures reliable operation. The number of gas and vapor tight joints is, of course, exactly cut in two.

While I prefer to operate converters in which the tubes depend from tube sheets it should be understood that the invention is in no sense limited thereto, and on the contrary converters can be used which are inverted. In such cases, of course, the tube sheet 2 has to bear the weight of the bath, and it is not as feasible to maintain a portion of the contact mass at a temperature considerably below that of the bath. For some reactions, however, this is not necessary, and the inverted design presents certain advantages. It, however, possesses a serious disadvantage in that it is difficult to fill the catalyst tubes without removing them, but such modified structures are included in the scope of the present invention.

In the drawing the tubes have been shown as round but any other shape, such as square, hexagonal, etc. may be employed where the conditions of operation make it desirable.

The process of the present invention and the apparatus is applicable generally to all reactions involving the transformation of carbon or nitrogen containing compounds. Thus, for example, the apparatus and process may be used for the reduction of organic nitro compounds to the corresponding amines, such as, for example, the reduction of nitrobenzol, nitrotoluol, nitrophenol, nitronaphthalene, and the like; reduction of phenol to cyclohexane, naphthalene to tetraline or decaline and benzol to cyclohexane, phthalic anhydride to phthalid or substituted or hydrogenated phthalids, crotonaldehyde to normal butyl alcohol, acetaldehyde to ethyl alcohol, maleic acid and its derivatives to the corresponding succinic acid derivatives, acetylene to ethylene, ethane and the like; many reactions involving the condensation of organic compounds, such as aldolizations, crotonizations, and the like may be carried out, as may esterifications of all types, etc.

Many reactions involving the splitting off of oxycarbon groups, such as the transformation of polycarboxylic acids or their derivatives to monocarboxylic acids, for example, the transformation of phthalic anhydride into benzoic acid in the presence or absence of steam or reducing gases; combined splitting and reduction reactions, such as the transformation of phthalic anhydride into benzaldehyde in the presence of reducing gases and the like.

The reduction of oxides of carbon to formaldehyde, methyl alcohol, methane, motor fuels and the like may also effectively be carried out by means of the present invention as can combined reductions of oxides of carbon coupled with reaction with other organic compounds of the most varied types.

The production of hydrocyanic acid from carbon monoxide and ammonia, and the like and 150

the oxidation of ammonia to oxides of nitrogen are other reactions for which the present invention is well suited.

The accurate temperature control and particularly the rapid cooling down of the reacted products makes the apparatus and process of the present invention particularly adapted to the oxidation of organic compounds, such as the oxidation of naphthalene to alphanaphthaquinone and phthalic anhydride; side chain compounds to the corresponding acids and aldehydes as, for example, toluol and its derivatives to the corresponding benzaldehydes and benzoic acids; borneol to camphor; isoeugenol to vanillin and vanillic acid; fluorene to fluorenone; phenanthrene to phenanthraquinone, diphenic acid and phthalic anhydride; anthracene to anthraquinone; benzol, phenol, tar phenols, etc. to maleic acid; furfural to maleic and mesotartaric acid; cresol to salicylaldehyde and salicylic acid; acenaphthene or acenaphthylene to acenaphthaquinone, bisacenaphthylidenedione, naphthaldehydic acid, naphthalic anhydride, and hemimellitic acid; methyl alcohol to formaldehyde, ethylene chlorhydrine to chloracetic acid and the like.

Organic oxidations in which undesired impurities are burned out may also most effectively be carried out by means of the present invention. Examples of such reactions are the purification of crude anthracenes with burning out of carbazole with or without removal of phenanthrene, purification of crude naphthalenes, crude mononuclear hydrocarbons, etc. The purification of coal tar ammonia by burning out organic impurities and sulfur compounds is another reaction very effectively carried out by means of the present invention.

While it will be seen that the present invention is applicable to a wide number of catalytic reactions in the vapor phase, the features of the invention render it peculiarly advantageous for reactions in which it is desirable to rapidly cool off reaction products in order to prevent further decomposition. This renders it particularly suitable for the oxidation of side chain compounds to aldehydes and acids, anthracene to anthraquinone, and particularly methyl alcohol to formaldehyde. Very delicate reactions, such as the oxidation of phenanthrene to phenanthraquinone, are also peculiarly adapted for the present invention.

What is claimed as new is:

1. A method of carrying out vapor phase catalyses involving the transformation of compounds of elements selected from the group having atomic numbers of 6 and 7, which comprises passing a gaseous mixture containing the vapors of compounds between a contact mass and a surrounding boiling bath liquid, the mixture

being in simultaneous direct heat exchanging relation with the contact mass and with the boiling liquid, but out of contact therewith and insulating the contact mass from direct heat exchange with the boiling liquid, reversing the flow of the reaction gas mixture and passing it through the contact mass on the reverse flow.

2. A method according to claim 1 in which the catalysis is the oxidation of an aromatic compound to quinone.

3. A method according to claim 1 in which the catalysis is the oxidation of anthracene to anthraquinone.

4. A method for carrying out vapor phase catalyses involving the transformation of compounds of elements selected from the group having atomic numbers of 6 and 7, which comprises passing a gaseous reacted mixture containing vapors of the compounds, around and in heat exchanging relation with rod-like masses of catalysts, continuing the flow around the catalyst rod and between it and the boiling bath liquid so that the reaction mixture is in simultaneous heat exchanging relation, but out of direct contact with the catalyst and boiling liquid, and serves to insulate the catalyst from direct heat exchange relation with the boiling liquid, reversing the flow of the reaction gases and causing them to pass through the above two referred catalyst rods on the reverse flow.

5. A method according to claim 4 in which the catalysis is the oxidation of an aromatic compound to quinone.

6. A method according to claim 4 in which the catalysis is the oxidation of anthracene to anthraquinone.

7. A method of carrying out vapor phase catalyses involving the transformation of compounds of elements selected from the group having atomic numbers of 6 and 7, which comprises passing a gaseous reaction mixture containing vapors of the compounds through a passage surrounding a body of contact mass and surrounded by a boiling liquid and out of contact but in direct heat exchange relation with both, reversing the flow of the reaction gas mixture and passing it through the contact mass on the reverse flow.

8. A method of oxidizing aromatic hydrocarbons, which comprises passing a gaseous reaction mixture containing vapors of the compounds through a passage surrounding a body of contact mass and surrounded by a boiling liquid and out of contact but in direct heat exchange relation with both, reversing the flow of the reaction gas mixture and passing it through the contact mass on the reverse flow.

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