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COMPLETE SPECIFICATION

Improvements in and relating to the Conducting of Chemical Processes and Apparatus therefor

We, JOHN BURNARD HARDING and CRAWFORD ALEXANDER CUNNINGHAM PETRIE, both British Subjects, both of Norton Hall, The Green, Norton-on-Tees, County Durham and IMPERIAL CHEMICAL INDUSTRIES LIMITED, a British Company, of Imperial Chemical House, London, S.W.1, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to processes of conducting in the liquid phase chemical reactions involving a gaseous reactant or reactants and apparatus therefor.

According to the present invention there is provided a method of conducting within controlled ranges of temperature and at superatmospheric pressure reactions which occur in the liquid phase between reacting substances of which one at least is a gas and one at least is a liquid under the desired reaction conditions, or of which all are gaseous under the said conditions and there is present also a liquid medium, the molar ratio of gas to liquid used being such that little vaporisation of the liquid occurs, which comprises, passing the reactants at a desired temperature and in desired proportions to a reaction zone containing a number of heat transfer coils, continuously passing through the coils per unit of time a volume of gas comprising at least one gaseous reactant obtained as hereinafter defined, which volume is at least equal to that of said gaseous reactant fed per unit of time to the reaction zone when measured under the same conditions of temperature and pressure, continuously mixing the streams of gas from the reaction zone and from the coils, together with make-up gas as desired, to obtain the gas for recycling to the reaction zone and to the coils, the temperature of the gas and the proportion of gas passed to the coils being selected to give the aforesaid controlled ranges of temperature in the reaction zone. An important application of the method is in processes operated under superatmospheric pressure of 50 atmospheres gauge and more.

When the gaseous and liquid streams to the reaction zone flow co-currently therein, preferably the reactants are introduced at, or near, the bottom of the reaction zone.

The process of the invention is of greatest value in relation to exothermic chemical processes. The coils in the reaction zone are then employed for cooling purposes, the gas taken off being cooled to the extent required by any suitable means, for example heat exchangers. The method of the invention is of special value in reactions in which control of temperature within very narrow limits is necessary, and then the temperature and proportion of the reactants should be closely controlled, preferably in automatic manner. Most frequently the gas fed to the reaction zone is preheated. The invention will now be described in relation to exothermic processes.

Examples of reactions to which the process of the invention may be applied are: liquid phase Fischer Tropsch reaction; synthesis of glycollic acid from aqueous formaldehyde and carbon monoxide; synthesis of propionic acid from ethylene, carbon monoxide and water; reductive alkylation of aromatic nitro-bodies and amines to give alkyl substituted amines, e.g. NN^1-dialkylphenylene diamines; and amination of high boiling aldehydes and ketones. Speaking broadly it may be applied advantageously to exothermic chemical reactions having heats of reaction of about 20 to about 200 kilo cals per gram. mole of product.

The criterion that little vaporisation of the liquid is permissible has the following significance. In reactions which take place predominantly in the liquid phase it is necessary for efficient operation that the reaction zone should contain as much liquid as possible compatible with there being sufficient gaseous reactant or reactants present for the reaction. If a large excess of gaseous reactant relative to the liquid were present in the reaction zone there would be the tendency for a considerable amount of the liquid burden to vaporise and leave the reaction zone as vapour. The material vaporised in this way would not be available for liquid phase operation (a disadvantage which would be aggravated when the liquid comprised a reactant) and consequently the over-all efficiency of the process would be considerably reduced. In reactions of this sort, therefore, little vaporisation of the liquid is permissible, and the aim is to conduct the reaction under such conditions that the minimum possible vaporisation of the liquid takes place.

However, control of the temperature within the reaction zone is needed, and with many reactions this control requires to be exercised within a very narrow range of temperature. But this control cannot be effected in the manner commonly employed in chemical processes, namely by increasing the volume of gaseous reactant relative to the liquid fed to the reaction zone, since, as indicated above, vaporisation of the latter would occur and adversely affect the reaction. According to the present invention, therefore, control is achieved by passing through coils situated within the reaction vessel a volume of gas per unit of time comprising at least one gaseous reactant which is at least equal to the volume of the gaseous reactant fed per unit of time to the reaction zone, said two streams of gas being both obtained from a common stream of gas prepared as herein described.

While the actual *modus operandi* will alter with the reactants, and especially with the heat of reaction, it will commonly be suitable to use a ratio, volume of gas passed through the coils per unit of time: volume of gas fed to the reaction zone per unit of time, of at least 3:1, measured at N.T.P. However, other factors permitting, it is preferred to conduct the process in such a way that this ratio is at least 9:1.

Having regard to the above discussion, the method of the invention is of particular application in exothermic processes for which the theoretical molar ratio of gas to liquid reactant required is in the order of from 2:1 to 4:1, and in which the actual ratio used for effective reactions is not higher than 7:1. However, the method of the invention may sometimes be used with advantage in processes in which the actual molar ratio of gas to liquid reactant employed amounts to as much as 5 times the molar ratio of gas absorbed in the reaction to liquid reactant by which it is absorbed.

If all the reactants are gaseous under the reaction conditions and consequently it becomes necessary to have an inert reaction medium present, then the molar ratio of gas to liquid is preferably chosen so that the reaction zone is substantially full of liquid phase and the gas rates are adjusted so that substantially no vaporisation of the liquid occurs.

The method is suitable in particular for the exothermic process comprising the carbonylation to oxygen-containing compounds, especially aldehydes, of mono-olefines containing from 2 to 18 carbon atoms, especially those containing up to 12 carbon atoms, and cyclohexene, by means of carbon monoxide and hydrogen e.g. at pressures of 200 to 300 atmospheres gauge and temperatures of 100° to 180° in the presence of a cobalt catalyst, which is preferably in dissolved form, for example as the salt of a fatty acid e.g. cobalt acetate, and more especialy as cobalt naphthenate. When mono-olefines containing from 2 to 5 carbon atoms are treated it is necessary or desirable to have present in the reaction zone an inert liquid medium, e.g. saturated butene trimer, an alcohol such as 3,5,5-trimethyl hexanol, or an ether such as dinonyl ether to provide the liquid phase. With C2 and C3 olefines the inert medium is necessary for liquid phase operation. While C4 and C5 olefines are liquid within partial ranges of the reaction conditions, it is nevertheless desirable with them to have an inert medium present in order to permit liquid phase operation throughout the range of reaction conditions. When the cobalt is present as a soluble compound a liquid inert medium or olefine is essential. When such an inert medium is employed and it is desired to hydrogenate the carbonylation product to alcohol subsequently, it is preferred to separate the medium from the hydrogenation product, e.g. as the bottoms obtained by distillation, and to return it to the carbonylation section. While from the reaction viewpoint, a wide range of H_2/CO mixtures can be employed in the process, e.g. molar ratios of from 1:1 to 4:1, it is preferred for best reaction to use a 1:1 molar rator of $H_2:CO$, which can be done if the reactor and auxiliary equipment are lined with a CO-resistant material such as copper. However, if ordinary steel equipment is employed it is desirable that this ratio should be not less than 2 : 1 and preferably about 3 : 1.

Preferably, the gas which has passed through the coils is subjected to treatment, for example in a heat exchanger, for removing sensible heat absorbed by it in its passage through the coils before being combined with the stream of gas from the reactor. Preferably, also, the exit gases from the reactor are cooled, e.g. by indirect heat exchange, and liquid product carried by them is removed in one or more catchpots and returned to the main stream of liquid reaction product. It will thus be seen that the circulating gas is divided into two streams, a reaction gas stream, which is fed to the reaction zone, and a cooling gas stream which is passed through the cooling coils situated in the reaction zone, and that these streams are combined on the exit side of the reactor and returned, together with make-up gas, for distribution as before between the reaction zone and cooling coils.

The cooling coils may comprise a large number of individual elements, which may be of any desired shape and length, but preferably are of considerable length, that is at least 3 times, and more preferably at least 6 times, the length of the reaction zone, in order to fill a large volume of the reaction zone. Preferably each element or pipe is connected at both ends to a common header. This arrangement has the advantage that by providing a large number of parallel paths for the cooling gas pressure drop, and therefore power expenditure, is considerably reduced. A preferred form of coil comprises a number of superposed serpentines connected by intermediate pipes, the whole being continuous throughout its length. Preferably 12 or more of these coils are employed, each connected at both ends to common headers suitably located in the apparatus. As a further preferred feature the coils are arranged so that each serpentine is staggered linearly or angularly with respect to the serpentines of the next adjacent coils. This arrangemnt provides a kind of network within the reactor and promotes mixing and contact of the reactants.

As a further preferred feature of the invention, the reaction vessel is fitted with a removable reaction basket of lesser diameter than the vessel and insulated from the walls thereof by a suitable insulating material, e.g. asbestos cement. This assembly has the advantage that stress is taken by the outer forging of the reaction vessel, which is kept cool by the insulation and therefore retains its strength, and that any corrosion which occurs tends to be limited to the basket, which can be readily removed and replaced, and does not affect the more expensive heavy forging itself. When a basket is employed the coils, in particular the serpentines, traverse substantially the whole width of the basket.

Preferably the gaseous reactants are fed to the bottom of the reactor by several pipes, although a single pipe may be used if desired. When a basket is employed, the pipes preferably pass down between the basket and the walls of the outer forging and are surrounded with the before-mentioned insulation.

Preferably the gas feed pipes are fitted with spargers or roses at the bottom. Preferably, also, they are provided with expansion compensating bends in the upper part of the reactor.

If all the reactants are normally gaseous at the reaction temperatures and pressures, it is necessary for liquid phase reaction to employ an inert liquid to serve as a reaction medium and this may be introduced at various points in the reactor but is preferably introduced near the bottom thereof.

The process in its preferred form provides the advantages that the temperature in the reaction zone can be maintained within narrow limits without introducing more gas directly to the reaction zone than is permissible for the reaction or reaction conditions, and that, by the use of the common headers and serpentines, pressure drop within the cooling system is kept to a minimum and reaction within the reactor is promoted by the intimacy of contact and mixing of the reactants brought about by the network of coils. Moreover, in previous processes separate coolant, e.g. a liquid, was circulated through coils situated in the reaction zone and connected to an independent heat removal system, but this either suffered from the disadvantage that the coils had to be sufficiently strong to withstand the high pressure obtaining in the reaction zone, and were therefore very heavy, inefficient thermally, and expensive; or that the external system had to be operated under the pressure obtaining in the reaction zone and this meant a relatively costly system including compressors. The disadvantages of using high pressure steam with its tendency for leakage are well known. In contrast with these processes the present process permits the use of efficient, relatively thin, coils and avoids the use of an additional high pressure system including compressors.

As another important feature the

invention comprises an apparatus adapted for conducting chemical processes of an exothermic or endothermic character under superatmospheric pressure. The apparatus comprises in its essentials a hollow reaction vessel capable of withstanding high pressures which, optionally, is provided with a removable reaction basket insulated from the walls of the reaction vessel by suitable insulation, and which is fitted with a number of coils, connected at their ends to common headers and isolated from the reaction zone, through which an indirect cooling medium can be circulated, thus providing a number of parallel paths, and is provided with feed pipes for the reactants delivering to the bottom of the reactor and with a take-off pipe or pipes for the liquid and gaseous products with intakes near the top of the reactor. There is a reactant gas recycle pipe line with branches on the feed side of the reactor for distributing gaseous reactant to the reaction zone through the said feed pipe or pipes and to the said coils through a header, and branches on the exit side of the reactor by which the gaseous product from the reaction zone through the said take-off pipe or pipes and from the coils through the header are received for recycling and distributing as before. Preferably, the cooling coils are in the form of separate lengths of piping of any desired shape or form connected at both ends to headers. More preferably each coil is of considerable length that is at least 3 times, in particular at least 6 times the length of the reaction zone, and comprises a number of serpentine coils, for example at least 4, connected by intermediate lengths of piping, the whole forming a continuous unit. Preferably, the number of parallel paths is the maximum possible since this gives the minimum pressure drop. In addition to removing heat of reaction the network of serpentines breaks up the gas bubbles and promotes reaction between the gaseous and liquid components. It is desirable to arrange the coils so that the serpentines are staggered linearly and/or angularly with respect to those of the next adjacent coils. In one arrangement for use with a 34′ × 4′ diameter reaction basket there are 13 parallel mild steel cooling coils each of $1^{3}/_{8}''$ outside diameter and 1″ nominal bore and comprising 13 serpentines. Neighbouring serpentines belonging to different coils are pitched with their axes at $2^{2}/_{5}''$ centres, and each serpentine is 33′ long.

This arrangement has the advantage that it promotes good mixing and contact of the reactants. By the use of apparatus of this kind the heat of reaction can be removed by indirect means in such manner that the temperature inside the reaction zone can be maintained within narrow limits, which is essential in many processes, and this can be achieved without introducing more gas directly to the reaction zone than is permissible for the reaction or the reaction conditions.

In using the apparatus for exothermic reactions it is preferably arranged that the cooling coil exit pipe feeds into the gaseous take-off line, that both include indirect heat exchangers and that the returned gas, together with needed make-up, is fed partly to the reactor through the gas feed line and partly to the cooling coils through a line leading to them.

A typical apparatus according to the invention is shown in vertical medial section in Fig. 1 of the drawings accompanying the provisional specification. 1 represents the reactor shell, which is a mild steel forging; 2, 2 two gas feed lines each provided with expansion bends 3 (actually there are seven gas feed lines in the apparatus, but for simplicity only two are shown); 3a the liquid reactant feed line with expansion bend 4 and sparger as shown; 5 the reaction basket (optional, but preferred), which is closed at top and bottom by end cover plates 6; 7 the individual cooling coils (of which there are thirteen but only three are shown for simplicity) each comprising six or seven serpentines 8 connected by intermediate lengths of piping 9, each individual coil being continuous throughout its length. The coils 7 lead through the end cover plates 6 to the common headers 10. The circulating cooling gas enters at 11 and leaves at 12, thus flowing co-current, inside the coils, with the direction of flow of the reactants. The liquid product is taken off by the pipe 13. In this particular form of apparatus the residual gas also leaves by pipe 13. 15 is a cylindrical stool for the basket. In this particular unit there is insulation between the reaction basket and the reactor shell, but this is not shown in Fig. 1 for simplicity.

The temperature is indicated by means of a sheathed thermocouple stretching to the bottom of the vessel, indicated by 14.

As described above, in the apparatus shown in Fig. 1 there are seven gas feed pipes, and these are distributed at equal distances round the circumference of the basket and are surrounded with insulation. However, the invention contemplates the use of any suitable number of gas and liquid lines as desired.

Fig. 2 shows a suitable form of serpentine coil in plan view, EXAMPLE.

Using the apparatus described, di-isobutylene was reacted in the liquid phase with carbon monoxide/hydrogen mixture containing 25% carbon monoxide by volume, at a total pressure of 250 atmospheres gauge and a temperature of 140°—170° C., in the presence of 0.1% of cobalt fed as naphthenate dissolved in the feed, and there was obtained a product comprising 3,5,5-trimethylhexanal-1 and 3,5,5-trimethylhexanol-1. The di-isobutylene and carbonylating gas feed pipes entered the top of the reactor and introduced the reactants to the reaction zone at the bottom of the basket.

The capacity of the converter was 5 cubic metres (176.8 cubic feet) and the rates of flow were approximately as follows, the gas volumes being measured at 20° C. and atmospheric pressure: 2.5 cubic metres (88.4 cubic feet) of liquid di-isobutylene per hour, 2500 cubic metres (88400 cubic feet) of carbonylating gas per hour, and 36000 cubic metres (1,271,160 cubic feet) of cooling gas per hour. In effect 1900 cubic metres (67089 cubic feet) of residual gas from the reactor together with 500 cubic metres (17680 cubic feet) per hour of hydrogen make-up and 270 cubic metres (9534 cubic feet) of carbon monoxide make-up are mixed with 36,000 cubic metres (1,271,160 cubic feet) of cooling gas comprising carbon monoxide and hydrogen, and the whole is recycled and distributed between the reactor and cooling gas circuits in the same proportions as before.

In the apparatus employed there were 13 cooling gas paths in parallel, each of $1^3/_8$" outside diameter and 1" nominal bore mild steel tubing and comprising 13 serpentines, one di-isobutylene feed pipe and 7 carbonylating gas feed pipes.

The carbonylating gas was fed to the reaction zone at a temperature of 140° C. and the gaseous reactants leaving the reaction zone were at 170° C.; the cooling gas entered the coils at 120° C. and left them at 155° C.; and after mixing these streams the cooled joint gas stream had a temperature of 105° C., rising to 120° C. after passing through the circulating pump. The reaction gas feed was preheated to 140° C. before entering the reaction zone.

As further features of the invention the apparatus and process are also applicable to endothermic reactions, provided the reaction temperature is not too high, in which case the procedure is to employ the same gas cycle and distributing system, but to pass heating gas through the coils instead of cooling gas. The circulating gases are heated in one or more heat exchangers. The reactants are preheated and brought together in the reaction zone, the temperature therein being controlled within the desired limits by controlling the temperature and quantity of gas passing through the coils.

As in exothermic, so in endothermic processes, the proportion of gas passing through the coils is preferably at least nine times that fed to the reaction zone, and the method of the invention is of particular value in processes in which the theoretical molar ration of reactant gas to reactant liquid is in the order of from 2:1 to 4:1, but does not exceed 4:1. It will be understood that in both types of process it is necessary to employ a proportion of gaseous reactant in excess of the stiochiometric amount in order to cause the reaction to proceed, and in practice, therefore, the molar ratio of gas to liquid may be as high as 7:1, but preferably should not exceed this.

If desired there may be a number of headers at each end of the coils, but this does not give as good results as a single header. It is of advantage to use a header of relatively large size.

In this specification by parallel paths is meant, by analogy with electrical terminology, paths between whose ends the same pressure drop exists.

Instead of a serpentine there may be used any other shape or form of coil having considerable length and adapted to pack conveniently with adjacent similar coils.

In the apparatus above described (4′ diam.) we have found good results are obtained using for each 2.4" depth of reaction space containing liquid a 33′ long $1^3/_8$" outside × 1" inside diameter mild steel serpentine pipe. For each such 2.4" depth the linear length of this pipe per square foot of cross-sectional area of the reactor approximately

$$=\frac{33}{\frac{22}{7}\times 2^2}=2.6'.$$

Most frequently, to achieve the benefits of the invention in major degree, it is desirable that this figure should not be less than 2.0 and preferable that it should be at least 2.6, especially when the reaction is highly exothermic. Hence, the heat transfer characteristics of the pipes employed for each 2.4" depth of reaction space should be at least equivalent to those of 2′ of the aforesaid mild steel pipe per square foot of cross-sectional area of reaction space, and preferably equivalent to more than 2.6 ft. per square foot similarly defined.

What we claim is:—

1. A method of conducting within controlled ranges of temperature and at superatmospheric pressure reactions which occur in the liquid-phase between reacting substances of which one at least is a gas and one at least is a liquid under the desired reaction conditions, or of which all are gaseous under the said conditions and there is present also a liquid medium, the molar ration of gas to liquid used being such that little vaporisation of the liquid occurs which comprises, passing the reactants at a desired temperature and in desired proportions to a reaction zone containing a number of heat transfer coils, continuously passing through the coils per unit of time a volume of gas comprising at least one gaseous reactant obtained as hereinafter defined, which volume is at least equal to that of said gaseous reactant fed per unit of time to the reaction zone when measured under the same conditions of temperature and pressure, continuously mixing the streams of gas from the reaction zone and from the coils, together with make-up gas as desired, to obtain the gas for recycling to the reaction zone and to the coils, the temperature of the gas and the proportion of gas passed to the coils being selected to give the aforesaid controlled ranges of temperature in the reaction zone.

2. A process as claimed in Claim 1 in which the coils form substantially a network in the reaction zone.

3. A method as claimed in Claim 1 or 2 which is operated in such manner that the gaseous and liquid streams to the reaction zone flow co-currently therein and the reactants are introduced at or near the bottom of the reaction zone.

4. A method as claimed in Claim 1, 2 or 3 when conducted at pressures of 50 atmospheres gauge or more.

5. A method as claimed in Claim 1, 2, 3 or 4 for conducting exothermic reactions in which the gas passing through the coils is employed to remove heat of reaction from the reaction zone.

6. A method as claimed in Claim 1, 2, 3, or 4 for conducting endothermic reactions in which the gas passing through the coils is employed to supply heat to the reaction zone.

7. A process as claimed in any of Claims 1 to 5 in which the volume of gas fed to the coils is at least nine times that fed to the reaction zone per unit of time, when measured under the same conditions of temperature and pressure.

8. A process as claimed in any of Claims 1 to 5 or 7 in which the theoretical molar ratio of reactant gas to reactant liquid is from 2:1 to 4:1.

9. A process as claimed in any of Claims 1 to 5 or 7 in which the actual molar ratio of gas to liquid does not exceed 7:1.

10. A process as claimed in any of Claims 1 to 5 or 7, 8 or 9, in which sensible heat absorbed by the gas in its passage through the coils is removed in at least one external heat exchanger.

11. A process as claimed in any of Claims 1 to 5 or 7 to 10 in which the exit gases from the reactor are cooled, and liquid product is separated from them in a vessel such as a catchpot.

12. A process as claimed in any of Claims 1 to 11 in which there are a number of coils traversing the reaction zone and these are connected at each end to common headers, thus providing a number of parallel gas paths through the liquid as hereinbefore defined.

13. A process as claimed in Claim 12 in which there are at least 12 parallel paths through the liquid.

14. A process as claimed in Claim 12 or 13 in which each path is at least 6 times the length of the reaction zone.

15. A process as claimed in any of Claims 12 to 14 in which each path is provided by a number of serpentine coils connected by intermediate pipes.

16. A process as claimed in Claim 15 in which each serpentine is staggered linearly and/or angularly with respect to the serpentines of the next adjacent coil.

17. A process as claimed in any of Claims 1 to 16 in which the reaction zone comprises a vessel provided with a removable reaction basket.

18. A process as claimed in any of Claims 1 to 5 or 7 to 17 for the carbonylation of mono-olefines containing from 2 to 18 carbon atoms, or of cyclohexene to oxygen-containing compounds by reaction thereof with gas mixtures comprising carbon monoxide and hydrogen.

19. A process as claimed in Claim 18 for the carbonylation of mono-olefines containing from 2 to 12 carbon atoms to oxygen-containing compounds.

20. A process as claimed in Claim 19 in which a temperature of 100° to 180° C., a pressure of 200 to 300 atmospheres gauge and a dissolved cobalt catalyst are employed.

21. A process as claimed in Claim 20 in which the mono-olefine contains from 2 to 5 carbon atoms and an inert liquid reaction medium is employed.

22. A method as claimed in Claim 6 or 6 together with any of Claims 12 to 17 in which the volume of gas fed to the coils is at least nine times that fed to the reaction zone per unit of time.

23. process as claimed in Claim 6 or 22 in which the theoretical molar ratio of reactant gas to reactant liquid is from 2:1 to 4:1.

24. A process as claimed in Claim 6 or 22 or 23 in which the actual molar ratio of gas to liquid does not exceed 7:1.

25. An apparatus adapted for carrying out exothermic or endothermic chemical processes conducted under superatmospheric pressure in the liquid phase between gaseous and liquid reactants or between two or more gaseous reactants, which comprises a hollow reaction vessel capable of withstanding high pressure, provided with feed pipes for the reactants and an off-take pipe or pipes for the products, and fitted with a number of coils, through which reactant gas can be passed as heat transfer medium, traversing the reaction zone and connected at their ends to common headers which are isolated from the reaction zone, and a reactant gas recycle pipe line provided with branches on the feed side of the reactor for distributing a gas comprising gaseous reactant to the reaction zone through the said feed pipe or pipes and to the said coils through a header, and branches on the exit side of the reactor by which the gaseous product from the reaction zone through the said off-take pipe or pipes, and from the coils through the header, are received for recycling and distributing as before.

26. An apparatus as claimed in Claim 25 adapted for operation in such manner that the gaseous and liquid streams to the reaction zone flow co-currently therein, which is provided with feed pipes feeding to or near the bottom of the reaction zone and with a gaseous and liquid product take-off pipe or pipes with their off-takes situated near the top of the reaction zone.

27. An apparatus as claimed in Claim 25 or 26 in which the coils form substantially a network in the reaction zone.

28. An apparatus as claimed in Claim 25, 26 or 27 provided with a removable reaction basket insulated from the walls of the reaction vessel by suitable insulation.

29. An apparatus as claimed in Claim 27 or 27 and 28 in which there is a large number of cooling coils each having a length at least 6 times that of the reaction zone.

30. An apparatus as claimed in Claim 29 in which each coil comprises a number of serpentines.

31. An apparatus as claimed in Claim 30 in which the serpentines are staggered linearly or angularly with respect to adjacent coils.

32. An apparatus as claimed in any of Claims 29 to 31 in which the thermal transfer characteristics of the coils per 2.4″ depth of reaction space are at least equivalent to those of 2 linear feet of mild steel pipe as hereinbefore defined per square foot of cross-sectional area of reaction space.

33. An apparatus as claimed in Claim 32 in which the said characteristics are at least equivalent to 2.6 feet/square foot of cross-sectional area of reaction space.

34. Apparatus as claimed in any of Claims 25 to 33 in which the gas recycle system is provided with heat exchangers and/or heating devices suitably situated.

35. Apparatus as claimed in any of Claims 25 to 34 characterised in that the off-take for the gaseous and liquid products is a single common pipe.

36. An apparatus adapted for carrying out exothermic or endothermic chemical processes conducted under superatmospheric pressure in the liquid phase between gaseous and liquid reactants or between two or more gaseous reactants, substantially as described by reference to the drawings accompanying the provisional specification.

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PROVISIONAL SPECIFICATION

Improvements in and relating to the Conducting of Chemical Processes and Apparatus therefor

We, JOHN BURNARD HARDING and CRAWFORD ALEXANDER CUNNINGHAM PETRIE, both British Subjects, both of Norton Hall, The Green, Norton-on-Tees, County Durham and IMPERIAL CHEMICAL INDUSTRIES LIMITED, a British Company, of Imperial Chemical House, Millbank, London, S.W.1, do hereby declare the nature of this invention to be as follows:—

This invention relates to methods of conducting exothermic or endothermic liquid phase reactions involving at least one gaseous reactant.

As one feature the invention provides a method of conducting exothermic reactions in the liquid phase, especially when carried out under superatmospheric pressure, e.g. at pressures in excess of 50 atmospheres gauge between reactants, of which at least one is gaseous, the proportion of gas to liquid being relatively small, which comprises continuously feeding the reactants at the desired temperature and pressure and in the desired proportions to, or near, the bottom of a reaction zone containing cooling coils, continuously circulating through the coils per unit of time a volume of a gaseous mixture, obtained as hereinafter defined and comprising a gaseous reactant or reactants, which is at least equal to that of said gaseous reactant or reactants required per unit of time for the reaction, continuously mixing the streams of gas from the reaction zone and from the cooling coils respectively, together with make-up gas as desired to obtain the gaseous mixture for circulating to the reaction zone and to the cooling coils, the temperature of the gas at any point in the system being controlled as desired. Most frequently the gas fed to the reaction zone is preheated.

Preferably, the proportion of cooling gas to reactant gas is at least 9:1 by volume measured at N.T.P.

The method is of particular application in processes in which, for example, the molar ratio of gas to liquid is in the order of from 2:1 to 4:1, but does not exceed 4:1.

Preferably, the gas which has passed through the coils is subjected to treatment, for example in a heat exchanger, for removing sensible heat absorbed by it in its passage through the coils before being combined with the stream of gas from the reactor. Preferably, also, the exit gases from the reactor are cooled, e.g. by indirect heat exchange, and liquid product carried by them is removed in one or more catchpots and returned to the main stream of liquid reaction product. It will thus be seen that the circulating gas is divided into two streams, a reaction gas stream, which is fed to the reaction zone, and a cooling gas stream which is passed through the cooling coils situated in the reaction zone, and that these streams are combined on the exit side of the reactor and returned, together with make-up gas, for distribution as before between the reaction zone and cooling coils.

The cooling coils may comprise a large number of individual elements, which may be of any desired shape and length, but preferably are of considerable length in order to fill a large volume of the reaction zone. Preferably each element or pipe is connected at both ends to a common header. This arrangement has the advantage that by providing a large number of parallel paths for the cooling gas, pressure drop, and therefore power expenditure, is considerably reduced. A preferred form of coil comprises a number of superposed serpentines connected by intermediate pipes, the whole being continuous throughout its length. Preferably 12 or more of these coils are employed, each connected at both ends to common headers suitably located in the apparatus. As a further preferred feature the coils are arranged so that each serpentine is staggered linearly or angularly with respect to the serpentines of the next adjacent coils. This arrangement provides a kind of network within the reactor and promotes mixing and contact of the reactants.

As a further preferred feature of the invention, the reaction vessel is fitted with a removable reaction basket of lesser diameter than the vessel and insulated from the walls thereof by a suitable insulating material, e.g. asbestos cement. This assembly has the advantage that stress is taken by the outer forging of the reaction vessel, which is kept cool by the insulation and therefore retains its strength, and that any corrosion which occurs tends to be limited to the basket, which can be readily removed and replaced, and does not affect the more expensive heavy forging itself. When a basket is employed the coils, in particular the serpentines, traverse substantially the whole width of the basket.

Preferably the gaseous reactants are fed to the bottom of the reactor by several pipes, although a single pipe may be used if desired. When a basket is employed, the pipes preferably pass down between the basket and the walls of the outer forging and are surrounded with the beforementioned insulation.

Preferably the gas feed pipes are fitted with spargers or roses at the bottom. Preferably, also, they are provided with expansion compensating bends in the upper part of the reactor.

If all the reactants are normally gaseous at the reaction temperatures and pressures, it is necessary for liquid phase reaction to employ an inert liquid to serve as reaction medium and this may be introduced at various points in the reactor but is preferably introduced near the bottom thereof.

The process in its preferred form provides the advantages that the temperature in the reaction zone can be maintained within narrow limits without introducing more gas directly to the reaction zone than is permissible for the reaction or reaction conditions, and that, by use of the common headers and serpentines, pressure drop within the cooling system is kept to a minimum and reaction within the reactor is promoted by the intimacy of contact and mixing of the reactants brought about by the network of coils.

As another important feature the invention comprises an apparatus adapted for conducting chemical processes of an exothermic character under superatmospheric pressure. The apparatus comprises in its essentials a hollow reaction vessel capable of withstanding high pressures which, optionally, is provided with a removable reaction basket insulated from the walls of the reaction vessel by suitable insulation, and which is fitted with a number of coils, connected at their ends to common headers, through which an indirect cooling medium can be circulated, thus providing a number of parallel paths, and is provided with feed pipes for the reactants delivering to the bottom of the reactor and take-off pipes for the liquid and gaseous products situated near the top of the reactor. Preferably, the cooling coils are in the form of separate lengths of piping of any desired shape or form connected at both ends to headers. More preferably each coil is of considerable length and comprises a number of serpentine coils, for example at least 4, connected by intermediate lengths of piping, the whole forming a continuous unit. Preferably the number of parallel paths is the maximum possible since this gives the minimum pressure drop. In addition to removing heat of reaction the network of serpentines breaks up the gas bubbles and promotes reaction between the gaseous and liquid components. It is desirable to arrange the coils so that the serpentines are staggered linearly and/or angularly with respect to those of the next adjacent coils. In one arrangement for use with a 34′ × 4′ diam. reaction basket there are 13 parallel mild steel cooling coils each of $1^3/_8''$ outside diameter and 1″ nominal bore and comprising 13 serpentines. Adjacent serpentines are pitched at 2 inch centres.

This arrangement has the advantage that it promotes good mixing and contact of the reactants. By the use of apparatus of this kind the heat of reaction can be removed by indirect means in such manner that the temperature inside the reaction zone can be maintained within narrow limits, which is essential in many processes, and this can be achieved without introducing more gas directly to the reaction zone than is permissible for the reaction or the reaction conditions.

In using the apparatus for exothermic reactions it is preferably arranged that the cooling coil exit pipe feeds into the gaseous take-off line, that both include indirect heat exchangers and that the returned gas, together with needed make-up, is fed partly to the reactor through the gas feed line and partly to the cooling coils through a line leading to them.

A typical apparatus according to the invention is shown in vertical medial section in Fig. 1 of the accompanying drawings, in which: numeral 1 represents the reactor shell, which is a mild steel forging; 2, 2 gas feed lines each provided with expansion bends 3 (actually there are seven gas feed lines in the apparatus, but for simplicity only two are shown); 3a the liquid reactant feed line with expansion bend 4 and sparger as shown; 5 the reaction basket (optional, but preferred), which is closed at top and bottom by end cover plates 6; 7 the individual cooling coils (of which there are thirteen but only three are shown for simplicity) each comprising six or seven serpentines 8 connected by intermediate lengths of piping 9, each individual coil being continuous throughout its length. The coils 7 lead through the end cover plates 6 to the common headers 10. The circulating cooling gas enters at 11 and leaves at 12, thus flowing co-current, inside the coils, with the direction of flow of the reactants. The liquid product is taken off by the pipe 13. 15 is a cylindrical stool for the basket.

The temperature is controlled by means of a sheathed thermocouple stretching to the bottom of the vessel, indicated by 14.

As described above, in the apparatus shown in Fig. 1 there are seven gas feed pipes and these are distributed at equal distances round the circumference of the basket and are surrounded with insulation. However, the invention contemplates the use of any suitable number of gas and liquid lines as desired.

Fig. 2 shows a suitable form of serpentine coil in plan view.

EXAMPLE.

Using the apparatus described, di-isobutylene was reacted in the liquid phase with a carbon monoxide/hydrogen mixture containing 25% carbon monoxide at a total pressure of 250 atmospheres gauge and a temperature of 140°—170° C., in the presence of 0.1% of cobalt fed as naphthenate dissolved in the feed. The di-isobutylene and carbonylating gas feed pipes entered the top of the reactor and introduced the reactants to the reaction zone at the bottom of the basket.

The capacity of the converter was 5 cubic metres (176.8 cubic feet) and the rates of flow were approximately as follows: 2.5 cubic metres (88.4 cubic feet of liquid di-isobutylene per hour, 2500 cubic metres (88400 cubic feet) of carbonylating gas per hour, and 36000 cubic metres (1,271,160 cubic feet) of cooling gas per hour. In effect 1900 cubic metres (67089 cubic feet) of residual gas from the reactor together with 500 cubic metres (17680 cubic feet) per hour of hydrogen make-up and 270 cubic metres (534 cubic feet) of carbon monoxide make-up are mixed with 36000 cubic metres (1,271,160 cubic feet) of cooling gas comprising carbon monoxide and hydrogen, and the whole is recycled and distributed between the reactor and cooling gas circuits in the same proportions as before.

In the apparatus employed there were 13 cooling gas paths in parallel, each of $1^{3}/_{8}''$ outside diameter and $1''$ nominal bore mild steel tubing and comprising 13 serpentines, one di-isobutylene feed pipe, and 7 carbonylating gas feed pipes.

The carbonylating gas was fed to the reaction zone at a temperature of 140° C. and the gaseous reactants leaving the reaction zone were at 170° C.; the cooling gas entered the coils at 120° C. and left them at 155° C.; and after mixing these streams the cooled joint gas stream had a temperature of 105° C., rising to 120° C. after passing through the circulating pump. The reaction gas feed was preheated to 140° C. before entering the reaction zone.

As further features of the invention the apparatus and process are also applicable to endothermic reactions, provided the reaction temperature is not too high, in which case the procedure is to employ the same gas cycle and distributing system, but to pass heating gas through the coils instead of cooling gas. The circulating gases are heated in one or more heat exchangers. The reactants are preheated and brought together in the reaction zone, the temperature therein being controlled within the desired limits by controlling the temperature and quantity of gas passing through the coils.

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678,211 PROVISIONAL SPECIFICATION

1 SHEET

This drawing is a reproduction of the Original on a reduced scale.

FIG. 1.

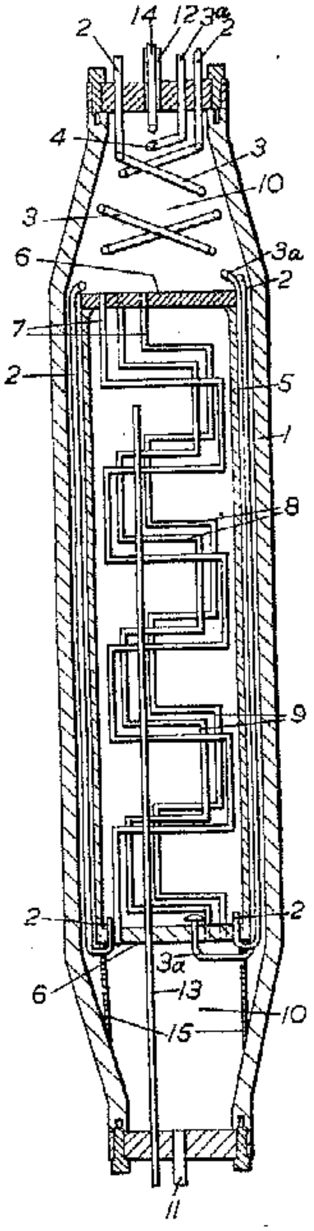

FIG. 2.