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UNITED STATES PATENT OFFICE

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METHOD OF CONTROLLING THE TEMPERATURE OF CHEMICALLY REACTING LIQUIDS

This invention relates to temperature control of reacting liquids, and especially to the control of exothermic gas-liquid reactions.

In many chemical reactions there is a tendency toward side reactions, or they tend to proceed in step-wise fashion beyond a desired intermediate product, and this is particularly true of reactions involving compounds of carbon. For example, in the partial oxidation of organic compounds the tendency is toward complete degeneration of the compound to carbon dioxide; and although usually the oxygen preferentially attacks a particular point in the molecule to predominantly produce a certain oxygenated product, it may, and usually does, enter the molecule at other points, although to a smaller extent under controlled conditions. Likewise, in chlorination and other operations similar to those referred to there are usually side reactions.

Such effects, unless minimized, may occur to such an extent as to render a given reaction commercially unrealizable, and thus to militate against processes which would otherwise be attractive. These tendencies, which are largely amenable to temperature control, are particularly predominant in the case of exothermic reactions, but they may occur in other cases.

Two general types of heat-controlling means have been used for the purpose of abstracting heat from such reacting systems, in order to maintain the material in the reaction zone at an optimum temperature at which a desired reaction predominates and undesirable effects are repressed. In one type a heat exchanging liquid is circulated through pipes disposed in the reaction zone, heat being transferred from the reaction zone through the pipe to the liquid. Considerable difficulty is presented by this type of apparatus in attaining accurate temperature control, especially where large amounts of heat must be absorbed, as in the case of highly exothermic reactions, or where large volumes of material react. This is due to the inherent difficulty of uniformly abstracting heat to maintain the body at proper temperature. These systems are not flexible, because they are not adapted to meet the changing conditions of most reactions, and as a result, they only approximate accurate temperature control.

In another type of heat controlling apparatus heat is transferred through a wall of a vaporizable liquid, heat being absorbed in vaporization of the heat exchanging liquid. Such systems possess some advantages over those just referred to, but in common with all prior systems they are open to a major disadvantage, namely, approximation rather than uniformity of temperature.

In all prior systems heat is transferred to a heat exchanging medium through a wall interposed between the two, and, except where the heated material is in an extremely thin layer, there will be a temperature gradient. For example, in all such apparatus the nature of the process is such that if the temperature of the reacting material at the wall is proper, material inwardly from the wall will be too hot. Or, where the heat absorption renders material centrally of the reaction zone at proper temperature, that at the wall is too cold. Consequently, maximum yields are not obtained, and other disadvantages of improper temperature control may be present. The usual practice, and the best obtainable with prior systems, is to maintain this unavoidable temperature gradient such that the average temperature will be optimum for the result sought, because commercial considerations render the ideally thin layer impracticable. For these and other reasons, temperature control of reacting systems has been imperfect because uniformity of temperature of the reactants was not attainable.

It is among the objects of this invention to provide a method of controlling the temperature of reacting liquids, and particularly of exothermic gas-liquid reactions, which is simple, highly efficient, readily practiced, eliminates the temperature gradient which prevailed in prior practice and provides substantially perfect uniformity of temperature throughout the liquid body, provides equally satisfactory control in large as well as small bodies of liquid, makes use of simple and readily available apparatus, and in the prac-

tice of which a change from control at one temperature to another is quickly and readily effected.

Other objects will be understood by those skilled in the art, and from the following description.

The accompanying drawing represents a vertical section through one form of apparatus which may be used in the practice of the invention.

In accordance with our invention, the temperature of a liquid body undergoing exothermic reaction with a gaseous reagent is controlled and uniformity of temperature throughout the body is attained by disposing the liquid body in a closed system, and maintaining such conditions of pressure in the system that vaporization of the liquid body or components thereof will absorb the heat of reaction. The amount of heat thus removed depends upon the amount of vaporization taking place.

In the processes according to this invention, a gas is used as one of the reactants, and consequently when working in a closed system under pressure, vaporization takes place into the inert, or unconsumed, fraction of the gas. Therefore, the amount of vaporization depends not alone upon the vapor pressure of the liquid, but upon the ratio of the vapor pressure to the total pressure. The vapor pressure is, of course, fixed by the temperature and the total pressure is the sum of the vapor pressure and the pressures of inert or unconsumed gas and volatile products of reaction, such as carbon dioxide or monoxide. Accordingly, the temperature of the liquid may be controlled by regulation of the pressure, whereby to control the vapor-inert gas ratio and thus to regulate the amount of vaporization, as will appear more fully hereinafter.

In accordance with the principles just enunciated, the system is maintained under such pressure that liquid will vaporize and absorb sufficient heat to maintain it at the proper temperature. In the practice of this invention, where inert or unconsumed gas is present, the total pressure will be greater than the vapor pressure of the liquid at reaction temperature, and it will usually be greater than the critical pressure of the compound, as will be explained more fully hereinafter. The vaporized liquid is condensed in the system and returned to the reacting body, so that during vaporization of liquid there is obtained an equilibrium condition.

The benefits of the invention are especially realizable when applied to highly exothermic reactions between a liquid and a gas, such as oxidations, chlorinations, and others, and it will be described with particular reference thereto.

The mechanism of the method provided by the invention may be understood by consideration of an oxidation reaction between a liquid compound and an oxidizing gas. All oxidations being exothermic, heat must be removed to maintain a proper temperature and prevent complete oxidation. In accordance with our invention, this heat is dissipated by vaporization and condensation of the compound, and we now believe that the following relations probably exist between the various factors, such as heat evolved, reflux and pressure.

In the simplest case of liquid-gas reaction, it is necessary to assume (1) an adiabatic system, (2) all oxygen reacting, (3) no gaseous or volatile products formed, (4) materials preheated to reaction temperature, and (5) liquid-vapor equilibrium.

In such a system, taking as a basis one mol. of oxygen reacting, let $Q=$ heat evolution per mol. of oxygen; $n=$ mols of liquid which must be vaporized to absorb this heat; $V=$ molal heat of vaporization of liquid at reaction temperature; $L=$ vapor pressure of the liquid; $P=$ total pressure; and $r=$ mols of inert gas to mols of oxygen. Then $Q=nV$, and

$$n = \frac{Q}{V} \qquad \text{Eq. 1}$$

and

$$\frac{L}{P} = \frac{n}{n+r},$$

so that by substitution from Equation 1

$$P = L\frac{Q+rV}{Q} \qquad \text{Eq. 2}$$

When air is used as the oxidizing medium, $r=3.76$, so that in such a case

$$P = L\frac{Q+3.76V}{Q}$$

From these equations it appears that the operating pressure on the system is determined by the heat to be removed by vaporization per mol. of inert gas. The vapor pressure of the liquid is determined by the operating temperature. The quantity n is, of course, fixed by the amount of heat to be removed, regard being had to its latent heat of vaporization, and where air is used, r is fixed. Accordingly, the variables are fixed for a given operating temperature and it is possible to calculate the pressure necessary in order that sufficient liquid will be evaporated to absorb the heat and maintain the liquid at temperature.

For example, assume that toluene is to be oxidized with air to benzoic acid, at 270° C. For purposes of calculation the following approximate values may be taken: $L=400$ pounds per square inch, $Q=100000$ cal. per

mol. O_2, and $V=6000$ cal. per mol. toluene. Then

$$P = 400 \times \frac{100000 + (3.76 \times 6000)}{100000} =$$
$$490 \text{ pounds per sq. in.}$$

Where the materials are not preheated, the pressure must be higher, as may be seen by Eq. 2, and assuming that 80 per cent of the heat is used in preheating:

$$P = 400 \times \frac{(0.2 \times 100000) + (3.76 \times 6000)}{0.2 \times 100000} =$$
$$850 \text{ pounds per sq. in.}$$

Likewise, the total pressure changes with change in the value of r. For example, using a gas containing 10 per cent of oxygen ($r=9$), and assuming that 85 per cent of the heat is used in preheating

$$P = 400 \times \frac{(0.15 \times 100000) + (9 \times 6000)}{0.15 \times 100000} =$$
$$1840 \text{ pounds per sq. in.}$$

This shows that the pressure increases as r increases, and at times it may be desirable or necessary to deviate from the r value of air. This may be accomplished readily, as by enrichment with pure oxygen, to decrease the ratio. And a suitable means of decreasing r is to dilute with an inert gas, for example by recirculation of oxygen-impoverished gas bled from the system.

the system in operation under the invention. If the pressure is too high an insufficient amount of liquid will be vaporized per mol. of gas reacting, and the temperature will rise until the ratio of L to P corresponds to equilibrium. If the pressure is too low, an excessive amount of liquid will be vaporized, and the temperature will be reduced. But by maintaining the pressure at that required by the operating conditions, the heat will be removed as rapidly as it is developed, and the temperature will remain constant. That is, with the pressure at the proper value, an increase in heat will simply cause more liquid to be vaporized, and the temperature will not change.

Except for the assumption that no gaseous products are formed, the assumptions upon which the derivation of the preceding equations is based are justified. Generally, however, gaseous products are formed, and in such a case a more complex equation may be used in calculating the pressure necessary to attain temperature control in accordance with our invention.

This modified equation is arrived at in the same manner as Eq. 2, where X=mols of volatile products per mol. O_2; S=mols liquid fed to the system per mol. O_2; Tr=reaction temperature; Tg and Tl=entering temperature of gas and liquid Cpg and Cpl=average molal heat capacity of gas and liquid.

$$Q = nV + (1+r)(Tr - Tg)Cpg + S(Tr - Tl)Cpl \quad \text{Eq. 3}$$

and

$$n = \frac{Q - (1+r)(Tr - Tg)Cpg - S(Tr - Tl)Cpl}{V} \quad \text{Eq. 4}$$

If heat losses from the system are high, the pressure necessary to maintain a given temperature will be higher than where the system is adiabatic, because so much liquid will be evaporated as to cool the liquid. On the other hand, with low heat losses, the pressure will still be above the vapor pressure of the liquid, as shown by Eq. 2. The operating (total) pressure may be reduced down to the vapor pressure at reaction tem-

and

$$\frac{L}{P} = \frac{n}{n + r + x},$$

so

$$P = L\frac{(n + r + x)}{n} \quad \text{Eq. 5}$$

and by substitution, and solving

$$P = L\frac{Q - (1+r)(Tr - Tg)Cpg - S(Tr - Tl)Cpl + rV + XV}{Q - (1+r)(Tr - Tg)(Cpg) - S(Tr - Tl)Cpl} \quad \text{Eq. 6}$$

perature by heat input to the system, because Q can thereby be increased to an infinitely large value. This, however, is scarcely desirable from an economical standpoint, and because for reasons of safety the air will not be preheated, the minimum pressure will normally be materially in excess of the vapor pressure.

The foregoing discussion indicates how the different variables affect the pressure on

The invention may be practiced in any suitable form of apparatus. The simplest form, which is shown in the drawing, comprises a lower reaction chamber 1 provided with a liquid inlet connection 2, and an upper refluxing portion 3 having means, such as an ordinary tube basket 4, for condensing vapors rising from the reaction zone and returning the liquid to the system. Water is circulated around the tubes of the condenser

by means of inlet and outlet connections 5 and 6. Chamber 1 is provided with means for heating the charge, such as an electric heater 7, and the reacting gas is introduced into the charge through a conduit 8, means such as a spreader dome 9 being preferably provided to distribute the gas uniformly through the charge. The apparatus is provided also with a pressure controlling valve 10, preferably one which automatically relieves the pressure at a predetermined value and whose blow-off valve is adjustable. A pressure gauge 11 may be provided for indicating the pressure in the system.

A suitable charge having been placed in chamber 1 and brought up to an appropriate temperature by means of the heater, the reacting gas is blown into the charge, and most suitably the gas is introduced substantially at the rate at which it is consumed. The pressure valve having been adjusted to bleed off inert gas at the proper pressure, the reaction proceeds smoothly, and accurate temperature control is provided. The process may be performed in continuous or in batch fashion. Where batch operation is used, the liquid may be withdrawn from connection 2. In continuous operation liquid is introduced continuously through inlet 2 and withdrawn in equal amount from an outlet 12. The reacted material may be cycled, or it may be worked up to separate the reaction products from unreacted liquid, the latter being returned to the system.

A particular benefit of the invention which is of equal importance with that of accurate temperature control, is that the entire body of liquid is maintained at a uniform temperature, because the combination of vaporizing liquid and gas bubbling through it insures almost perfect temperature distribution.

The benefits of the invention may be shown by tests which we have made in connection with its application to oxidation of aromatic compounds. In these tests, an apparatus similar to that described was used, air being used as the oxygen-containing gas. In these tests toluene was cycled continuously through the reactor. The results are shown in the following table:

	Temperature °C.	Press. sq. in.	Inlet O₂ mol. percent	Oxygen converted to		
Liquid treated				Benzoic acid, percent	Benzaldehyde, percent	CO₂ percent
Toluene	310	1000	5.9	22.6	5.6	10.3
Toluene	290	1000	26.8	18.8	2.9	13.3
Toluene	220	1000	31.2	26.6	1.9	21.6

Other tests have shown that at 1000 pounds pressure and with inlet oxygen of about 35 mol. per cent, conversion efficiencies substantially like those of the 220° C. example are obtained when using air-nitrogen and air-carbon dioxide mixtures, providing the reaction temperature is kept between about 255 to 270° C. This shows the beneficial effect of an inert diluent in reducing the heating effect.

Other substances may also be oxidized in this manner to produce useful partial oxidation products. For example, phthalic anhydride may be made from naphthalene, and our experiments have shown that other cyclic compounds such as cyclohexane, o-cresol, and xylene may be converted similarly to oxygenated compounds. The invention is equally applicable to other processes which can be effected in the liquid phase.

It will be observed that oxidation of toluene in the liquid phase has been effected directly by molecular oxygen without the aid of a catalyst. Heretofore such liquid phase processes required the production of oxygen in statu nascendi, or, in the case of vapor phase processes, catalysts have been essential. The disadvantages of such processes are well known, and the superiority of the present process not only resides in effecting uniform and accurate temperature control, but also in realizing reactions which heretofore were carried out imperfectly or under disadvantageous conditions.

A modification of our process resides in the use of an auxiliary heat exchanging liquid in cases where the vapor pressure of the liquid undergoing reaction is insufficient for the purposes of the invention. In most cases this will be unnecessary, but where it becomes desirable to augment the liquid vapor pressure, this may be done by adding as a component of the liquid phase a liquid material whose vapor pressure increases or substantially entirely effects the desired pressure. Such a liquid should be inert, miscible with the material to be oxidized, and it should possess a high vapor pressure at, and its critical temperature should lie above, the reaction temperature. For this purpose water will be suitable in many instances, because its vapor pressure is high at elevated temperatures, its critical temperature is above that which will usually be necessary, and it has a high latent heat of vaporization. In most cases water will be formed in oxidizing reactions, but until it has accumulated after considerable reaction its effect will normally be low. Such materials do not take part in the reaction, and are used for their heat-exchanging effect. In other reactions some other heat-exchanging liquid may be desirable or necessary owing to particular conditions, and these are within the knowledge of those skilled in the art. For example, carbon tetrachloride possesses many properties which adapt it for this use in chlorination reactions.

According to the provisions of the patent

statutes, we have explained the principle and operation of our invention, and have illustrated and described what we now consider to represent its best embodiment. However, we desire to have it understood that, within the scope of the appended claims, the invention may be practiced otherwise than as specifically illustrated and described.

We claim:

1. A method of carrying out an exothermic liquid-gas reaction, comprising passing said gas into the liquid in a closed system, and regulably controlling vaporization of the liquid by regulation of the total pressure on the system, whereby to maintain the liquid uniformly at reaction temperature, said pressure being greater at all times than the vapor pressure of the liquid at said temperature.

2. A method of carrying out an exothermic liquid-gas reaction, comprising passing said gas into the liquid in a closed system, and by regulation of the total pressure on the system controlling the amount of vaporization and maintaining the liquid at reaction temperature, said pressure being greater at all times than the vapor pressure of the liquid at said temperature, and condensing the vaporized liquid in and returning it to the system.

3. A method of controlling an exothermic liquid-gas chemical reaction, comprising passing the gas into the liquid in a closed liquid-vapor system, and absorbing heat from the liquid to maintain the entire body of liquid uniformly at reaction temperature by vaporization and condensation of liquid in the system, the vaporization being effected by regulation of the total pressure on the system in accordance with the formula

$$P = L\frac{Q + rV}{Q}$$

where P is the total pressure necessary to effect said vaporization, L is the liquid vapor pressure at reaction temperature, Q is the molal heat of reaction per mol. of reacting gas, r is the ratio of mols reacting to mols inert gas, and V is the molal heat of vaporization of the vaporized liquid.

4. A method of carrying out an exothermic liquid-gas chemical reaction, comprising passing the gas into the liquid in a closed liquid-vapor system, and maintaining the liquid uniformly at reaction temperature by regulating the concentration of reacting gas and by regulated vaporization of liquid, the vaporization of the liquid being controlled by maintaining a total pressure on the system greater at all times than the vapor pressure of the liquid at said temperature, and the vaporized liquid being condensed in and returning it to the system.

5. In an exothermic chemical reaction between a liquid and a gas in a closed liquid-vapor system, the method of maintaining the liquid uniformly at reaction temperature, comprising regulating the ratio of vapor to inert gas by subjecting the system to a total pressure in excess of the vapor pressure of the liquid at reaction temperature to cause removal of heat by vaporization of liquid, and condensing the vaporized liquid in the system.

6. A method according to claim 5, in which the gas concentration is regulated by recirculation of the gas drawn from the system.

7. A method of controlling an exothermic reaction between a reacting liquid and a reactive gas to be introduced into said liquid, comprising passing said gas into a liquid phase including said reacting liquid and an inert heat exchanging liquid in a closed system, regulating the total pressure on the system to regulate the amount of vaporization and thereby to uniformly maintain said liquid phase at reaction temperature, and condensing vaporized liquid in the system, said pressure being at all times substantially in excess of the vapor pressure of the liquid.

8. A method of controlling an exothermic liquid-gas reaction, comprising passing an oxidizing gas into a liquid body of the material to be oxidized and an inert heat exchanging liquid of greater volatility than said material in a closed system provided with refluxing means, and by regulation of the total pressure controlling the ratio of vaporized liquid to unconsumed gas in the vapor phase to maintain the liquid body uniformly at reaction temperature, said pressure being substantially in excess of the vapor pressure of the liquid.

9. A process according to claim 8, said heat exchanging liquid being water.

In testimony whereof, we hereunto sign our names.

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