

Safe Scale-Up of Oxidation by Hydrogen Peroxide in Flammable Solvents

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Abstract:

Oxidation of species by hydrogen peroxide gives rise to the potential to release oxygen, which in the presence of flammable solvents can lead to an explosion risk due to the extreme sensitivity to ignition of the resulting oxygen-enriched atmosphere. The release of oxygen gas in the form of bubbles from the liquid can produce an electrostatic field, which is capable of igniting sensitive flammable atmospheres in larger-scale operations. A method of inerting the system can be applied which makes the atmosphere nonflammable and the reaction safe, whilst minimising solvent losses. A practical scale-up from laboratory flask to pilot scale of 150 kg demonstrated that solvent losses, whilst significant, are not a barrier to production of fine chemical intermediates on a commercial scale.

Introduction

Hydrogen peroxide is known for its strong oxidising properties, but there are occasions where there is a release of gaseous oxygen from the reaction mixture due to the simple decomposition of the peroxide. Where there are solvents used in the preparation, flammable atmospheres may be present; thus there is a risk of a fire or explosion occurring. This is rarely a problem in small-scale laboratory preparations typically undertaken in research facilities, but when scaling up to large processes, care is needed because of the risk of ignition. This is because the action of the bursting bubbles can generate electrostatic charge, and in a large vessel this can have enough energy to ignite an oxygen-enriched solvent vapour atmosphere. Unless the release of oxygen can be avoided, it is necessary to ensure that the oxygen is diluted to a concentration less than that which will support combustion to avoid the formation of a flammable atmosphere. The dilution can be effected by the use of an inert gas purge fed over the surface. The flow rate required can be calculated from the maximum gas release rate determined by small-scale experiments.

The Hazard

There is a previously reported incident¹ where decomposing hydrogen peroxide in a tank released oxygen, and the solvent vapour in the tank ignited. This was investigated by Pratt² who concluded that the mechanism was that the bursting bubbles formed highly charged droplets and the corona discharges from the resultant electrostatic field ignited

the vapour in the atmosphere in the tank. The mechanism of corona-type discharges from bubbles was first investigated by Blanchard³ and later by Nifuku et al.,⁴ and the generated charge was found to be similar to that which formed coronas. The magnitude of the charge on the individual droplets was found to be substantially independent of the liquid, that is water was just as bad as ethyl alcohol and kerosene. However, for a conducting solvent, the effective earth plane of the liquid made the field strength self-limiting. This was not the case with insulating solvents such as gasoline and kerosene which were used for the experiments. The field strength from bubbles bursting above water was found to be in excess of 100 kV/m; thus above an insulating solvent, a higher field-strength would be possible.

The generation of such high field-strengths in a laboratory-sized flask of about 250 mL does not present a risk of ignition, simply because the maximum surface potential of the liquid in the flask is restricted by the size of the flask. The risk of ignition due to high surface potentials was investigated by Walmsley,⁵ who suggested a safe limit of about 60 kV for the surface potential of the liquid. Jones and Bond⁶ investigated the space potential of an electrostatic field in the centre of a vessel for avoiding the ignition of a vapour–air mixtures and considered a safe maximum was about 25 kV, on the basis of a uniform electrostatically charged fine droplet mist. However, if this is compared to a linear field strength from a high surface potential to vessel wall at earth potential, then a centre-space potential of 25 kV corresponds to a surface potential of 50 kV, which is the same order of magnitude as Walmsley proposed. For a laboratory-scale flask, the linear dimension from liquid surface to vessel wall is about 50 mm, so that the surface potential for a field strength of 100 kV m⁻¹ is 100 kV m⁻¹ × 0.05 m = 5 kV, which is very low, so that the risk of an incendive electrostatic spark discharge occurring would be very low also. If this is compared with a pilot-plant scale vessel, with, say, a 500 mm headspace, then the surface potential would increase by a factor of 10, making a discharge possible. Although the presence of the earthed agitator shaft down the centre of the vessel will tend to reduce the maximum surface potential, the effect of this is difficult to predict, and therefore it is best to take the worst case and assume that it does not reduce the maximum surface potential that could occur.

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Effect of Oxygen Enrichment

Thus far, the effect of the electrostatics has been considered. There is a further complication concerning the electrostatic discharges and their incendivity or propensity to ignite flammable atmospheres. A typical hydrocarbon solvent, such as hexane, has a minimum spark ignition energy of about 0.25 mJ,⁷ this being the energy required to ignite the optimum mixture in air. Work by Litchfield⁸ shows that the minimum ignition energy of methane dropped from 0.3 mJ in air to 0.0027 mJ in oxygen. The minimum ignition energy of other hydrocarbons exhibited similar reduction ratios of typically 100-fold in oxygen. A similar reduction is given by Haase⁹ for diethyl ether from 0.19 to 0.0012 mJ. However, other data on minimum ignition energies in oxygen are sparse. Whilst the minimum ignition energy is likely to be reduced by a large factor of probably 2 orders of magnitude, it would also suggest that the maximum safe surface potential would reduce in proportion, so thereby the risk would appear to increase with increases in both oxygen concentration and vessel size.

Hence, the problem is that the potential enrichment of the vapour space by oxygen from decomposing hydrogen peroxide reduces the ignition energy of the solvent vapour, while the bubbles of oxygen bursting at the surface produce an electrostatic field sufficient to ignite the more sensitive mixture. Therefore, ignition is a distinct possibility in larger vessels. Clearly, if the oxygen content of the vapour phase is below that required for combustion, then propagation of flame through the bulk of the vapour space cannot occur. Thus, if the oxygen is kept below the minimum oxygen for combustion, typically about 8–10% v/v for solvents, by feeding in an inert gas at an adequate rate, an explosion is impossible. However, if the oxygen is reduced to just 21%, that is, the equivalent of air, the bulk of the vapour phase will be flammable but not unduly sensitive to ignition. Whilst this would appear to solve the problem, each bubble bursting at the surface is oxygen-rich and solvent-saturated and thus is extremely sensitive to ignition, and since the bursting of the bubble can provide sufficient energy to ignite it, it also acts as the ignition source. Any ignition of a single bubble would then propagate through the entire vapour space, resulting in an explosion.

Basis of Safety

From the foregoing, it can be seen that the only possible basis of safety is to ensure that the vapour space is nonflammable. To calculate the required inert gas flow (in our case nitrogen) to dilute the vapour space to a suitably low oxygen concentration, say 5% v/v oxygen, it is necessary to determine the gassing rate under experimental conditions. The reaction should be prepared in a small-scale laboratory reaction vessel of 200 mL, operated as an adiabatic calorimeter¹⁰ fitted with a gas buret,¹¹ so that the maximum rate of oxygen evolution can be determined. This is scaled up

for the batch size envisaged on the pilot-plant scale. As the intention is to reduce the pure oxygen evolution to less than 5% v/v of oxygen, an inert gas flow of 19 times that of the oxygen evolution would be required. Clearly, for other oxygen levels, the flow rate is adjusted appropriately.

The mixing of the inert gas with the atmosphere in the vessel would appear to be a potential problem because, if the mixing is poor, there may be inadequate dilution of the oxygen. In trials of purging small vessels with nitrogen, it was established that the oxygen level leaving the vessel decreased almost exactly as would be the case for a perfectly mixed system, providing the feed rate of inert gas was greater than 10 volume changes per hour. The calculation for this is given elsewhere.¹² As the actual purging time follows the theoretical time assuming perfect backmixing, it was concluded that there would be good mixing of the incoming nitrogen with the oxygen, without the need for a subsurface sparge.

Potential Problem with Inert Gas Purging

Clearly the addition of so much nitrogen to a vessel containing a flammable solvent is likely to evaporate a quantity of the solvent. On a laboratory scale this would be inconsequential, but on a pilot-plant scale, the loss could have significant potential emissions to atmosphere as well as financial penalties. To estimate the potential loss, two approaches were taken.

First, a grossly pessimistic approach was taken that the gas leaving would be saturated with the solvent vapour. As the nitrogen is a noncondensable gas, the overall heat transfer coefficient of the condenser would be very low due to attempting to condense in the presence of noncondensables, and hence solvent losses could be expected to be high.

The second approach was to estimate the likely loss due to evaporation into the gas stream, using an empirical equation due to Clancy.¹³ This equation assumes a linear velocity across the surface of a circular pool, and hence simplifying assumptions have to be made as to the likely velocity of the gas across the liquid surface. The assumptions made were that the gas flow was parallel to the liquid surface, and the linear velocity was assumed to be twice the volumetric flow rate divided by the cross-sectional area in the vertical plane of the ullage space of the vessel. This is likely to be somewhat less than the mean velocity, but is simple to calculate, and the factor of 2 was chosen to take some account of the increase of velocity at the entry and exit points. By choosing other criteria for the velocity, almost any evaporation rate less than the saturation value could be calculated.

Minimising the Loss

Clearly the inert gas flow has to be maintained at all times during the potential for the release of the oxygen; thus, unless

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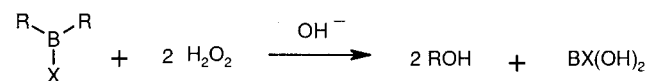
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the reaction is known to be complete, it is not safe to stop the inert gas flow to minimise the evaporative loss of solvent. The ideal approach would be to actually monitor the oxygen concentration leaving the reactor, so that if the release of oxygen increases for any reason, the inert gas flow is increased to compensate, and vice versa. Whilst this is ideal, the vessel used was not equipped with such oxygen-monitoring equipment nor could it be fitted quickly enough for production purposes.

The approach taken by our chemists was to add the peroxide at a rate commensurate with a realistic inert gas flow and a suitable rate for the oxidation reaction to take place. This was to add the peroxide over a period of 2 h. At the end of the addition period, the batch was sampled and a peroxide test paper used to quantitatively determine the excess peroxide concentration. The paper used (Quantofix Peroxid 100) was calibrated to detect peroxide down to 1 mg L⁻¹ in steps of 1, 3, 10, 30, and 100 mg L⁻¹. The peroxide concentration is measured to determine the point at which the inert gas flow can be stopped. This is discussed later.

The nominal oxygen concentration within the ullage space was restricted to 5% v/v to ensure that this was well below the minimum oxygen required for the combustion of the solvent, which had a calculated minimum oxygen for combustion of 11% v/v. Allowing a suitable margin of safety, the maximum oxygen concentration could be allowed to rise to, say, 8% v/v, still allowing a margin before the vapour space became flammable. Thus, there is an allowable increase of 3% v/v. This can be equated to a volume of pure oxygen, which again can be equated to the hydrogen peroxide concentration which could release this quantity of oxygen from the batch. Hence, there is a lower limit of peroxide concentration in the batch below which the oxygen released will not increase the vapour space above 8% v/v oxygen. Once the peroxide concentration is below this value, the inert gas flow can be stopped, as the remaining oxygen cannot make the vapour space flammable. However, as the oxygen is evolved from the batch, some is likely to dissolve in the liquid and may be released later when the batch is heated. In our case, the solution was held at a temperature close to the boiling point, so that the potential for oxygen to remain in solution would be low. For other reactions, the potential for dissolved oxygen to be released will need to be considered on a case-by-case basis.

A Case Study



The above methodology can be illustrated with a case study. The oxidation of a dialkyl borane can be achieved by the use of hydrogen peroxide. The procedure used is to

dissolve the alkyl borane complex in a suitable solvent in a basic medium and add an excess of hydrogen peroxide to promote the reaction. The oxidation proceeds to oxidise the carbon–boron bonds to form the ROH. This results in the R alcohols remaining in the organic phase, and the boronic acid and salts partitioning into the alkaline aqueous phase, making the separation of the product from the boron-containing byproducts a simple physical separation.

However, the use of the excess hydrogen peroxide at high pH releases oxygen gas, which would enrich the atmosphere to an oxygen content well above that of air. A small-scale batch was prepared using a sealed vessel connected to a gas buret to determine the rate of gas evolution. With the maximum release rate of oxygen determined, the inert gas flow could be calculated to reduce this to less than 5% v/v. On the scale used in our facility, it corresponded to a flow of 8.55 m³ h⁻¹ of nitrogen. This allowed a 150 kg preparation to be undertaken for trial manufacture of a fine chemical.

At the scale we proposed, the total loss of solvent calculated on the basis of the gas stream leaving fully saturated with solvent would equate to about 6 kg h⁻¹ on a 150-kg batch size. Using the Clancy equation and the assumptions described above, a loss of 0.5 kg h⁻¹ was estimated. During plant trials purging inert gas over solvent alone, the loss was measured at only 1.4 kg h⁻¹, which was found to be acceptable. Similar losses were found during the actual manufacture of a batch on 150 kg scale.

Conclusions

(1) The use of hydrogen peroxide for oxidation of organic species can release oxygen. (2) Oxygen-enriched flammable atmospheres are very sensitive to ignition. (3) The corona discharge from the bursting of bubbles in the liquid can have sufficient energy to ignite an oxygen-enriched atmosphere. (4) The risk of ignition increases with the ullage space of the vessel used for the reaction. (5) A basis of safety can be provided for the use of hydrogen peroxide in the presence of flammable solvents. (6) The rate of oxygen evolution needs to be determined accurately to determine the rate of inert gas required to keep the atmosphere nonflammable. (7) The use of an inert gas purge to dilute the oxygen ensures safe operation of the process. (8) In a process at 150 kg scale, the solvent losses are manageable and tolerable and have been estimated reasonably well at about 25% of the loss on the basis of saturation of the inert gas with solvent.

Acknowledgment

I thank the Directors of Avecia Limited for their kind permission to publish this paper, and the valuable contribution made by the Chemists and Chemical Engineers in Avecia Process Technology.

Received for review July 29, 2002.

OP025574Y