THE EXPLOSIVE DECOMPOSITION OF ETHYLENE OXIDE VAPOUR UNDER PRESSURE, PART II

By J. H. BURGOYNE, D.Sc., Ph.D., C.Eng., M.I.Chem.E.,*† K. E. BETT, B.Sc., Ph.D., C.Eng., M.I.Chem.E.,* and RICHARD LEE, B.Sc., Ph.D.*‡

SYNOPSIS

The explosive decomposition of ethylene oxide vapour has been investigated with initial conditions in the range 20 to 100°C and up to 135 lbf/in^2 abs pressure. Explosion pressures have been observed with improved dynamic recording methods and the explosion products analysed by gas chromatography, whereby the pressure development on explosion has been fully accounted for. Suppression of the explosion by nitrogen has been further studied and shown to be temperature-dependent. Previous apparently discordant results at different temperatures have thus been reconciled. The suppressing effects of carbon dioxide, steam, and ammonia—like that of nitrogen—have been shown to be explicable simply in terms of their thermal capacities. Added methanol and propylene oxide however are decomposed in the explosion flame and exert a more complex effect.

Introduction

That pure ethylene oxide vapour, at atmospheric pressure and temperatures above the normal boiling-point (10·7°C) can propagate a decomposition flame was shown by Burden and Burgoyne in 1949.[1] From the products obtained by upward flame propagation in a closed, 2 in. diam tube the decomposition reactions appeared to be represented by:

$$C_2H_4O = CO + CH_4 + 32{\cdot}0 \text{ kcal/mole} \quad (1)$$

$$C_2H_4O = CO + \tfrac{1}{2}C_2H_4 + H_2 + 8{\cdot}0 \text{ kcal/mole} \quad (2)$$

$$C_2H_4O = CO + \tfrac{1}{2}C_2H_6 + \tfrac{1}{2}H_2 + 24{\cdot}0 \text{ kcal/mole} \quad (3)$$

Reaction (1) was responsible for 50·2% of the decomposition and reaction (2) for 23·3%. Reaction (3) occurred to a very small extent and the rest of the ethylene oxide remained undecomposed. The incompleteness of the decomposition could be due to condensation of the saturated vapour on the cold walls of the tube by compression resulting from flame propagation, and to their flame-quenching effect on a propagation that was clearly but marginally possible. The flame would not propagate downwards in the closed tube and it appeared that in a vessel in which the source of ignition was not at the lowest point the flame decomposition at atmospheric pressure and temperature could be far from complete.

Gerstein, McDonald, and Schalla[2] measured the burning velocity (normal velocity of the flame relative to the unburnt vapour) of pure ethylene oxide vapour under conditions similar to those used by Burden and Burgoyne. The value obtained, although relatively low (12·5 cm/s), was beyond theoretical expectation and it appeared that in the vertical tube upward flame propagation was assisted by convective flow of the hot products. Taking advantage of the highly-organised flow conditions of the Egerton-Powling flat-flame burner,[3] Friedman and Burke[4] succeeded in stabilising a decomposition flame in an upward-flowing stream of ethylene oxide vapour at atmospheric pressure thus demonstrating that the difficulty concerning downward propagation of the decomposition flame in an ordinary tube or vessel probably arises from gas dynamic effects. That this should be so is not surprising when the very low value of their measured burning velocity (2·7 cm/s) is considered—a value that is in good agreement with theoretical expectation, having regard to the thermochemical effect of the reactions shown above as they participated under Friedman and Burke's conditions.

Studies by Friedman and Burke of the effect of increasing pressure and temperature on the burning velocity of the ethylene oxide flame were capable of interpretation on the assumptions that pressure favoured reaction (1) above, whilst temperature (pre-heat) favoured the less exothermic reaction (2). Investigations into the decomposition explosion in a closed vessel, under initial pressure were first made by Hess and Tilton[5] who operated in a range of initial conditions of 40–45°C and 45–85 lbf/in^2 abs. An electrically-heated platinum wire was employed as the direct source of ignition or as the igniter of a charge of mercuric fulminate which in turn initiated flame in the ethylene oxide vapour. The ability of various added gases to suppress the decomposition explosion was studied but in presenting their findings regarding the proportions of these gases necessary for this purpose Hess and Tilton assumed that the values were independent of initial temperature and pressure.

Burgoyne, Bett, and Muir[6] extended the work of Hess and Tilton using an initial temperature of 125°C and ethylene oxide vapour pressures up to 155 lbf/in^2 abs. An electrically-fused wire, of proven igniting ability, was used as the source of ignition. The suppression of the decomposition explosion by added gases was investigated, particular attention being paid to nitrogen. It was found that the proportion of added gas requisite for complete explosion suppression increased with increasing initial pressure of the ethylene oxide vapour. This is in accordance with the conclusion of Friedman and Burke that the decomposition becomes more exothermic with increasing pressure assuming that the effect of the added gas is in relation to its thermal capacity. It appeared, on the other hand, that an increase in initial temperature had only a slight effect on the ease of suppression and this was qualitatively understandable in the light of the conclusion of Friedman and Burke that pre-heat favoured the less exothermic mechanism of decomposition. On the assumption of a small temperature effect however, the work of Burgoyne, Bett, and Muir indicated a considerably greater requirement of added gas for complete explosion suppression at a given vapour pressure of ethylene oxide than did that of Hess and Tilton. A major purpose of the work now to be reported was

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* Department of Chemical Engineering and Chemical Technology, Imperial College, London, S.W.7.

† *Present address:* 3/5 Dowgate Hill, London, E.C.4.

‡ *Present address:* Kowloon, Hong Kong.

to resolve this discrepancy and to extend the range of added gases or vapours considered to cover some of those with which ethylene oxide may make contact in contemporary processes of chemical synthesis. These include some additives that may not remain chemically inert in the presence of the ethylene oxide decomposition flame. In such cases, their suppressive effect may be expected to depend, not upon their thermal capacity but upon the thermochemistry of their decomposition and reactions with ethylene oxide or its decomposition products.

Experimental

Apparatus and procedure

The stainless steel explosion vessel employed was that previously used by Burgoyne, Bett, and Muir.[6] It had an internal volume of 148·9 in^3 in the form of a cylinder 4·5 in. diam and was designed to withstand dynamic pressures up to 1500 lbf/in^2 gauge. The technique of filling the vessel with known mixtures of ethylene oxide vapour and other constituents under prescribed temperature and pressure conditions was as previously described,[6] as was the method of ignition of the prepared mixture.

The method of recording the explosion pressure was however considerably improved. A piezo-electric type of pressure transducer was employed which when tested dynamically using shock-tube techniques showed a linear characteristic within $\pm 1\%$. In view of this it was assumed that the transducer responded correctly under conditions of dynamic loading, and it was used to test the capacitance-type transducers previously used. It was found that the 0–1500 lbf/in^2 gauge measuring gauge used by Burgoyne, Bett, and Muir read low by comparison and it may therefore be that some of their explosion pressure measurements were in error.

The explosion products were analysed quantitatively using a standard Beckman C.C.2 gas chromatograph. The columns used were as follows:

(1). An 8 ft silica gel column, Davidson 28–200 mesh, at 70°C, for carbon monoxide, methane, ethane, carbon dioxide, and propylene.

(2). A 6 ft column of Carbowax 400 supported on 42–60 mesh Teflon for ethyl alcohol, ethylene oxide, propylene oxide, water, and benzene.

(3). A 12 ft column of 20% cetyl alcohol on alkaline washed embacel, 60–100 mesh, at 40°C for ammonia and amines.

A molecular sieve (5A) column was used to detect oxygen.

Results

EXPLOSIVE DECOMPOSITION OF PURE ETHYLENE OXIDE VAPOUR

TABLE I.—*The Effect of Initial Pressure on Gaseous Products of Decomposition of Ethylene Oxide Vapour at 100°C*

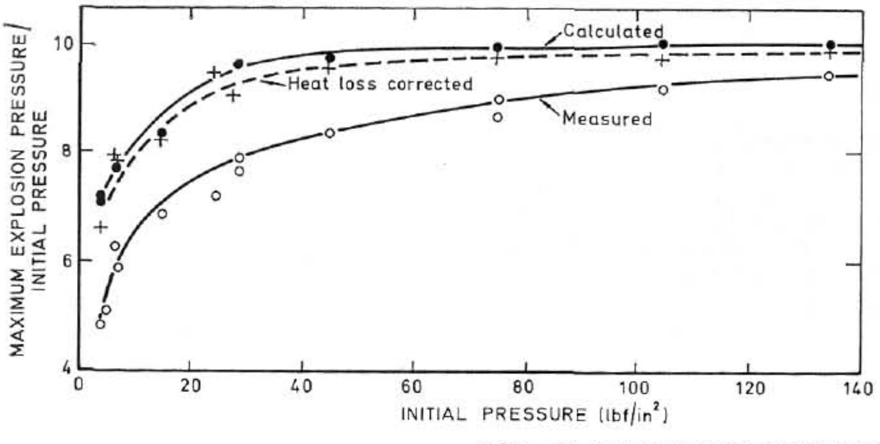
(*products in vol.%*)

	Initial pressure = 4·66 lbf/in^2 abs	Initial pressure = 14·7 lbf/in^2 abs	Initial pressure = 74·7 lbf/in^2 abs
Ethylene oxide (vol %)	2·62	0·90	0·44
Methane (vol %)	20·95	27·80	28·10
Carbon monoxide (vol %)	44·10	46·15	43·40
Hydrogen (vol %)	23·15	22·20	27·52
Ethane (vol %)	1·08	0·50	0·11
Carbon dioxide (vol %)	—	0·10	0·20
Ethylene (vol %)	8·00	1·91	0·11
Benzene (vol %)	—	0·44	0·12

The explosive decomposition of pure ethylene oxide vapour was studied over an initial temperature range of 20 to 100°C and an initial pressure range up to 135 lbf/in^2 abs. Analyses of the gaseous products of decomposition at 100°C and three different pressures are shown in Table I. Solid carbon was also formed in each explosion. It was found that, at 100°C, flame propagation was not possible with an initial pressure below 4·16 lbf/in^2 abs.

It will be seen from Table I that the proportion of ethylene oxide remaining undecomposed is greater with lower initial pressures. Reduction in initial temperature produced a similar, but more marked effect, and with 20°C and 14·7 lbf/in^2 abs the proportion was as high as 36%. The ethylene oxide that did decompose, however, yielded similar products at 20°C as at 100°C, apart from a slightly reduced methane yield. Change in initial pressure, on the other hand, caused more difference, the reaction to ethylene being favoured at lower, and that to methane at higher pressures. An increase in surface/volume ratio for the explosion vessel, produced by the addition of liners, gave increased yields of ethylene and ethane at the expense of hydrogen and methane.

On the basis of the products found after explosion at 100°C and various pressures up to 135 lbf/in^2 abs, maximum explosion pressures were calculated on the assumptions of no heat loss from the system and no dissociation of products. These are expressed, as the ratio maximum explosion/initial pressures, by the " calculated " curve in Fig. 1, and compared with the " measured " curve relating to the observed values. To the latter have been applied a simple correction for heat loss in the experimental vessel, derived from the cooling curve succeeding maximum pressure in each explosion pressure-time record. The results are depicted by the " heat loss corrected " curve. It appears therefore that the shortfall in the measured explosion pressures is mainly accountable by



Exploding wire ignition
● : calculated values
+ : values corrected for heat loss
○ : measured values

Fig. 1.—*The effect of the initial pressure on the ratio of explosion pressure to initial pressure for ethylene oxide vapour at 100 °C*

heat loss during the explosion, although if product dissociation at the flame temperature had been taken into account in reaching the " calculated " curve, the discrepancy could well have been even less. The results as a whole indicate that at the higher pressures the pressure increase ratio tends to a constant value which, even in the absence of heat loss (*i.e.* in large vessels) seems unlikely to exceed ten for an initial temperature of 100°C. If it were supposed that the decomposition proceeded exclusively and adiabatically by the most exothermic course—reaction (1)—the pressure increase ratio should not exceed 10·6 at this initial temperature.

With variation in initial temperature, the explosion pressure ratio passes through a peak. For an initial pressure of 14·7 lbf/in^2 abs this peak occurred at 60°C and had a value of 7·6 (uncorrected for heat loss) in the experimental vessel. The explanation appeared to be that as the initial temperature dropped below 60°C the proportion of ethylene oxide undecomposed increased, as previously noted. Above this temperature the amount of undecomposed material became less significant but the effect of increasing initial temperature in reducing the density of the original vapour came into play so reducing the explosion pressure relative to the initial pressure in the usual way.

The rapid increase in the proportion of ethylene oxide remaining undecomposed with initial temperatures below 60–80°C was traced to the condensation of the saturated vapour on the relatively cold vessel walls due to compression in advance of the explosion flame. In these circumstances the condensed material remained undecomposed but was revaporised by the hot explosion products.

With initial temperatures in excess of 80°C the explosion pressure (for the range of initial pressures employed in this work) was insufficient to cause vapour condensation. In this temperature range there was evidence that the (relatively small) amount of ethylene oxide remaining undecomposed in the explosion was attributable to flame-quenching within a " dead-space " adjacent to the vessel walls.

EFFECT OF ADDED INERT GASES

The admixture with ethylene oxide of a sufficient proportion of inert gas makes it non-explosible under given initial conditions. Measurements have been made of the relative amounts of nitrogen, steam and carbon dioxide required for this purpose over the ranges of initial temperature and pressure already defined.

In any particular case the relative amount of added gas required for suppression was judged from the effect of progressive additions on the explosion pressure ratio. It was found that the pattern followed was the same for the three gases considered. The first additions produced a linear drop in the ratio to a value of about 5·2, whereupon there was a sudden drop to about 1·5 and a slow tailing-off to unity. The proportion of additive which caused the sudden drop was taken as the practical explosion limit for the case concerned.

The effect of addition of inert gas on the decomposition products was similar in the three cases. The first linear fall in the explosion pressure ratio was mainly attributable to the replacement of ethylene oxide by inert gas in the initial mixture. At the sharp fall the amount of ethylene oxide decomposed diminished drastically. However, in relation to the ethylene oxide actually decomposed, the yield of carbon monoxide remained constant to the limit whilst hydrogen and free carbon formed fell steadily. The yield of methane at first rose but, as the limit was approached, it fell off, accompanied by a rise in the yields of ethylene and (though less) ethane. At the limit the distribution of decomposition products was the same irrespective of which inert gas was used.

A series of measurements at various temperatures and pressures with nitrogen as the additive in the explosion vessel with and without liners, showed that the limit was the same for internal diameters of 4·5 and 3·75 in., but was reduced appreciably for 1·5 in. It was concluded therefore that in the vessel without liners (diameter 4·5 in.) the limit value was not being significantly influenced by heat loss, or other wall effects, and so was representative of the value for larger vessels still. Limit data subsequently presented were obtained under this condition.

In Fig. 2 are plotted curves relating to various initial temperatures which show the proportion of added nitrogen necessary to suppress explosion as a function of the initial vapour pressure of ethylene oxide in the mixture. The curve determined by Burgoyne, Bett, and Muir[6] at 125°C is included and conforms with the new results. It is seen that there is a considerable effect of initial temperature on the nitrogen requirement at any pressure, and the major discrepancy between Burgoyne, Bett, and Muir[6] and Hess and Tilton[5] is immediately explained. In fact, a plot of the nitrogen limit requirement against temperature at a series of initial pressures shows a linear relationship.

The total pressure to which a storage vessel containing liquid ethylene oxide must be pressurised with nitrogen so as to dilute the vapour above the liquid sufficiently to make it non-explosible at various storage temperatures is shown in Fig. 3. The line AB represents the limit conditions calculated from the experimental results in Fig. 2, but it is recommended that the total pressure above the ethylene oxide be increased to that given by line CD so as to ensure that the vapour contains 10% more nitrogen than the limit requirement at all temperatures. It may be seen from Fig. 3 that the 35% nitrogen recommended[7] on the basis of Hess and Tilton's work[5] (theoretical limit 25%) would be insufficient to suppress an explosion at storage temperatures in excess of 28°C.

A limited number of measurements using carbon dioxide additional to ethylene oxide at a vapour pressure of 25 lbf/in^2 abs gave the limits shown in Table II.

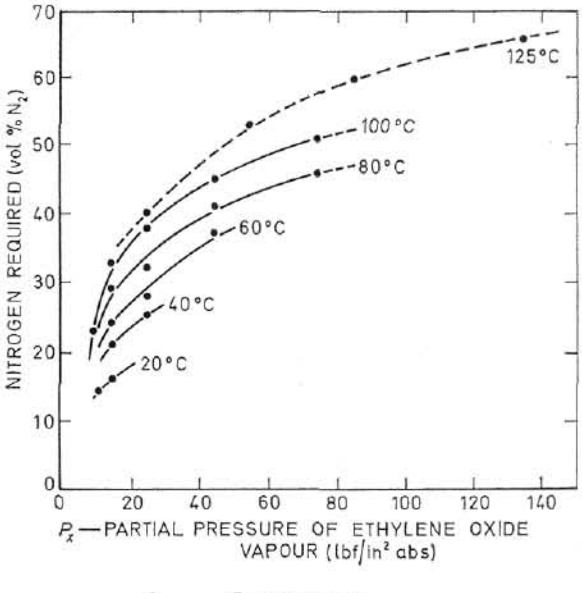


Fig. 2.—*The effect of the initial vapour pressure of ethylene oxide on the proportion of nitrogen required to suppress explosion at various temperatures*

TABLE II—*Effect of Initial Temperature on the Proportion of Carbon Dioxide Required to Suppress the Explosion of Ethylene Oxide Vapour at 25 lbf/in² abs*

Initial temperature (°C)	Carbon dioxide (vol % of total mixture)
42	17
59	20
80	23
100	26

A single measurement with steam as the additive, at 100°C and a vapour pressure of ethylene oxide of 25 lbf/in² abs gave a limit of 32 vol % of the total mixture. A comparison of this result with those for nitrogen and carbon dioxide under the same initial conditions revealed that the calculated adiabatic explosion temperatures for the three limit mixtures were substantially the same. From this result, which might be expected so long as the additives do not enter into reaction with the decomposing ethylene oxide, it follows that the molar ratio of additive to ethylene oxide at the limit is inversely proportional to the molar specific heat of the added gas. The limit requirement of any other inert gas of known specific heat under the same initial conditions can therefore be calculated.

Furthermore, the work with added nitrogen at different temperatures showed that at a given pressure the limit composition varied so as to maintain a nearly constant calculated adiabatic explosion temperature. This result enables the effect of temperature upon the limit at a certain pressure to be predicted. No simple relationship exists between the limit and the initial pressure, but from the data for nitrogen limit requirements in Fig. 2 requirements of other inert gases of known specific heat can readily be calculated throughout the range of initial temperature and pressure covered.

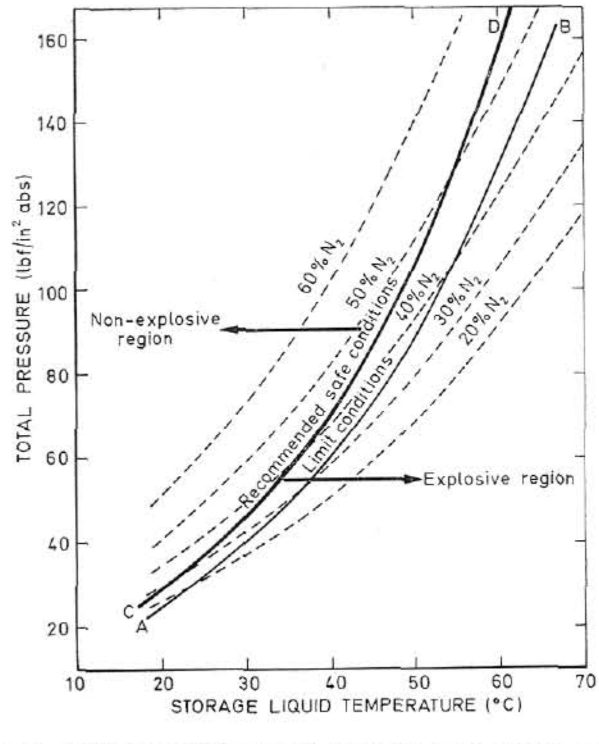


Fig. 3.—*Pressure to which a vessel containing liquid ethylene oxide must be pressurised with nitrogen to ensure that the vapour is non-explosible*

THE EFFECT OF THE ADDITION OF POTENTIALLY REACTIVE MATERIALS

Of the additives so far considered steam might be considered to be possibly reactive in the explosion flame. As has been shown, however, it appeared to behave simply as an inert material, exerting a flame-suppressing influence solely by virtue of its thermal capacity. Three other materials that may come into contact with ethylene oxide in its role in chemical synthesis were also examined, namely methanol, propylene oxide, and ammonia. Of these only ammonia showed signs of reacting appreciably with ethylene oxide in the prepared mixture prior to explosion testing, and steps were taken in this case to reduce the time of prior contact.

At a temperature of 100°C and a vapour pressure of ethylene oxide of 25 lbf/in² abs the proportions of the added materials necessary to suppress explosion were as shown in Table III. The inert gases are included for comparison.

Ammonia was found to behave in every respect as an inert additive. The effect on product yields was similar to that of nitrogen, the ammonia itself emerging unchanged from the explosion products. The calculated adiabatic temperature at the limit was as for the inert additives and hence its effect was predictable simply on the basis of its thermal capacity.

Both methanol and propylene oxide were decomposed in the explosion flame yielding in each case one mole of carbon monoxide additional to that derived from the ethylene oxide for each mole of additive. At the limit, the adiabatic flame temperature was less for methanol (1170°K), and more for propylene oxide (1420°K) than for the inert additives (1230°K). From this it would appear that methanol has a small promoting influence and propylene oxide an inhibiting influence upon the ethylene oxide decomposition explosion.

Conclusions

1. At low pressures and temperatures the explosive decomposition of ethylene oxide, subject to a source of ignition, is incomplete. In small vessels heat losses reduce the pressure rise due to explosion. The indications are, however, that at an initial temperature of 100°C the ratio of maximum explosion/initial pressure is unlikely to exceed ten in large vessels, over the range of pressure investigated. Above 100°C, the pressure ratio decreases owing to the reduction in initial density of the vapour; and although the ratio may increase below 100°C, below about 60°C incompleteness of decomposition rapidly reduces it.

2. The proportion of added nitrogen required to suppress the explosion increases with increasing temperature and pressure. The change with temperature is such as to maintain

TABLE III—*Proportions of Added Vapours and Gases to Suppress the Explosion of Ethylene Oxide Vapour at 100°C and 25 lbf/in² abs Vapour Pressure*

Additive	Limit addition (vol % of total mixture)
Methanol	16
Ammonia	24
Propylene oxide	25
Carbon dioxide	26
Steam	32
Nitrogen	37

a constant flame temperature at the limit but no simple relation has been found to express the effect of initial pressure.

3. The suppressing effects of inert gases are directly attributable to their thermal capacities. Limiting additions of carbon dioxide, steam, and ammonia can be calculated from the data for nitrogen on the basis that for a given vapour pressure of ethylene oxide the limit flame temperature is independent of the nature of the added gas.

4. The effect of additives that decompose rapidly at the flame temperature is more complex. Methanol suppresses at a lower limit flame temperature, as compared with an inert additive whilst with propylene oxide the effect is in the reverse direction.

Acknowledgments

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DISCUSSION

The CHAIRMAN (Mr. R. J. Kingsley) said that the work reported was a great comfort to all who worked in this field, and it was interesting and gratifying how much has been filled in as against the position ten years ago when, apart from the work of Hess and Tilton, there really was no guidance at all.

He asked if the authors would say a little more about the Antwerp explosion, upon which the dusts of time had now settled to some extent, which had been most serious, and had led to considerable loss of life. There might be lessons in it, particularly concerning the pumping of ethylene oxide.

Dr. BURGOYNE replied that what he would say was a matter of his own opinion and there was room for other opinions. However, he had investigated the explosion in some detail and, as he saw it, it consisted essentially of explosive decomposition in a vessel, of full capacity of two tons, containing about one ton of liquid ethylene oxide. It was in fact a reflux receiver containing the liquid essentially at its boiling-point under a pressure of 4 or 5 atm. It appeared that decomposition was initiated in a rotary pump that followed this vessel and on the outlet of which there was a control valve which, at the particular moment, was closed for a time by the operation of the level–control system of the reflux vessel. It appeared that there has been some fouling in the pump which had recently been down for maintenance and that caused overheating and decomposition in the pump itself which was full of stationary liquid under the conditions mentioned. In some way, through a boiling ethylene oxide liquid/vapour mixture, an explosive decomposition propagated back and established in the bulk storage vessel. He was satisfied, from a study of the effects of the explosion, and having regard to the energy that the system contained, that most of the ethylene oxide in the vessel participated in the explosive decomposition. He thought that the lesson was that an unstable liquid like ethylene oxide should not be allowed to become stationary in an operating pump.

Dr. J. R. GROVE said that it had been mentioned that with the limiting mixtures of ethylene oxide with different gases, the flame temperature was substantially constant. Did that apply to the mixture with nitrogen, although there were different starting temperatures? Was the final flame temperature constant in those conditions?

Dr. BURGOYNE replied that the theoretical flame temperature at the limit composition was independent of the initial temperature.

Dr. GROVE asked if that could therefore be applied to other systems to correct critical compositions, for starting temperature on similar systems.

Dr. BURGOYNE replied that he thought so. The important thing was that the diluent was truly inert, that it did not react with thermochemical effect, either on itself or with the explosive medium.

The CHAIRMAN asked if the authors would care to expand a little on the treatment of propylene oxide/ethylene oxide vapour mixtures which were of interest to some delegates present.

Dr. BURGOYNE replied that he and his co-workers had not done a great deal of work on propylene oxide additions. In Table III of the paper there was a statement of the propylene oxide limit addition where the initial temperature was 100°C, with 25 lbf/in^2 abs initial vapour pressure of ethylene oxide; 25% of propylene oxide sufficed to suppress that explosion. That was the only actual limit measurement they had made. Propylene oxide decomposed in an ethylene oxide explosion but so far as they had been able to discover, within certain limits of temperature and pressure, propylene oxide alone did not propagate an explosive decomposition. The thermochemical effect of the decomposition of propylene oxide in the ethylene oxide explosion complicated the extrapolation of the limit data. He thought that some extrapolation could be made though not perhaps with the confidence that one did with inert diluents.

It was, however, possible to say that the addition of propylene oxide could make the ethylene oxide system safe by the fact of a limiting addition of propylene oxide above which the system was non-explosive, but the detailed investigation had been limited.

The CHAIRMAN said that a point which he thought would be of interest was what the final pressure to initial pressure ratio was likely to be for propylene oxide concentrations of less than 25%, compared to the value of 10% which they seemed to approach in general for pure ethylene oxide, because that obviously had a bearing on the design of reactors for such systems. Was it likely to be greater or less, or was it likely to be greater immediately below the 25% and less thereafter?

Dr. BURGOYNE replied that the limits had been taken where there was a sharp drop in the pressure increase ratio to a value near to unity. Immediately below the limit addition of additive, a pressure increase ratio of 5 would be typical. From there it increased almost linearly to the value for the undiluted ethylene oxide.

The CHAIRMAN said that he thought that the relevant point was whether at any stage it was likely to rise above 10, which was what one designed for with pure ethylene oxide.

Dr. BURGOYNE replied that he did not think it was likely to rise above that.

Mr. J. R. CROWTHER asked what method of heating was used—was it by immersion in an oil bath or with the use of electrical winding?

Dr. BETT replied that it was heated in an electrically-heated air bath. The entire vessel was heated in that fashion.

Mr. CROWTHER said that that explained the heat losses.

Dr. BURGOYNE said that the heat losses to which he had referred were from the explosion flame to the walls of the vessel—short-term loss from the explosion—and the correction was made for this from the cooling curve immediately after the completion of the explosion.

Mr. CROWTHER said that he was interested in the steam diluent. He had used carbon dioxide and nitrogen: he was not familiar with the use of steam. He would like the authors to enlarge on this. He was interested in the steam at the pressures the authors were talking about, and the temperatures—namely 100 lbf/in^2 and possibly 40°C. The authors referred to steam—did they mean a water vapour?

Dr. BURGOYNE replied that it was water vapour *i.e.* dry steam. That was potentially reactive with ethylene oxide.

Dr. BETT said that there had not been reactions during the periods prior to ignition when the two were in contact but if they remained in contact for longer periods of time, a chemical reaction would take place.

Dr. BURGOYNE said that that was the trouble about steam; it could not really be used as a permanent diluent because of reaction. It could be used in an emergency but long-term contact would result in reaction.

Mr. CROWTHER stated that he would not consider it on those terms. That was why he was surprised that it had been mentioned. He had used the other two which were totally unreactive.

The CHAIRMAN said that he thought that the addition of steam even in emergency would not be good practice. He recalled that a reaction between water and ethylene oxide did take place given sufficient pressure so that additional heat might be generated.

On the question of storage, the storage graph referred to total pressure: he took this to mean total pressure including diluent pressure.

Dr. BURGOYNE thought it would be better to put steam in the category of potentially reactive additives in the paper. There were situations where they came together in certain processes and one needed the information for assessing explosibility in these circumstances.

The total pressure was ethylene oxide vapour pressure plus partial pressure of the diluent.

Mr. D. G. FURZEY referred to the point raised about the possibility of ethylene oxide condensation on the wall of the vessel due to the pressure of the explosion front. He asked if the authors could give a little information on the conditions required to explode the liquid material.

Dr. BURGOYNE replied that anything he thought he knew about it really arose from the Antwerp experience when it appeared that there was a transmission of vapour decomposition to liquid decomposition and it seemed to him that this occurred through the boiling mixture. He thought that between the point of initiation and the large storage of bulk liquid there was a boiling liquid in the pipeline and it seemed feasible that the vapour decomposition should transmit to the liquid—or could transmit to the liquid—through the boiling mixture.

Mr. B. J. PRIESTLEY said that the condensing liquid obtained in the authors' experiments surely had the same properties as the boiling liquid in the explosion. There had been no transference of the explosion to the liquid in the experimental work. He would have thought that the two were very similar.

Dr. BURGOYNE said that in the Antwerp explosion there was thought to have been a system where the vapour and the liquid were rather intimately mixed, *i.e.* a boiling liquid. The interfacial area between liquid and vapour would be much greater than with vapour condensing on the walls of the explosion vessel.

Mr. PRIESTLEY said that therefore, for a very large vessel where there might be condensation of droplets in the actual vapour, as opposed to, in the other case, droplet formation on the walls, the explosion might be transferred to the droplets giving a liquid explosion. Presumably the explosion could be transferred to the bulk liquid by a similar mechanism.

Dr. BURGOYNE agreed that, if the interfacial area was great enough, that could be so.

Mr. M. KNEALE said that if it were postulated that a large volume of ethylene oxide was burning at atmospheric pressure was there a likelihood of the liquid detonating or exploding in some way?

Dr. BURGOYNE said that there was no experience of liquid ethylene oxide exploding at atmospheric pressure so far. If a situation could be conceived where ethylene oxide was burning under a considerably elevated pressure, then it might be so.

The CHAIRMAN pointed out that it had happened in the present case.

Dr. J. R. GROVE asked whether in this particular case of ethylene oxide decomposing in large volume the release of energy was so fast that the actual decomposition of the liquid in the liquid phase had to be assumed, or could it all boil off and decompose in the vapour?

Dr. BURGOYNE said that the evidence was against a liquid-phase detonation and in favour of a rapid decomposition. He thought that decomposition of the liquid must be involved but that it did not follow that all the decomposition was in the liquid phase.

The CHAIRMAN said that there seemed to him to be two clear lessons. One was that the temperature at which ethylene oxide was pumped should be monitored; secondly, that flow control systems involving a control valve on the discharge of a pump delivering ethylene oxide without some permanent recycle should be avoided.

Dr. BETT said that he thought it true to say that no one in the laboratory had made liquid ethylene oxide explode. Perhaps the conditions they used were not sufficiently stringent.

Mr. A. D. CRAVEN wondered if it was possible that ethylene oxide was similar to ammonium nitrate in that it was not possible to make very small amounts explode in the laboratory because a large critical mass was required. In the case of the tank explosion there was such a large critical mass.

Dr. BURGOYNE replied that that might be true. There had been explosions of liquid ethylene oxide on a smaller scale in storage cylinders. The reaction started as catalysed polymerization and self-accelerated into decomposition.

Dr. D. J. LEWIS asked how it was established, in the Antwerp case, what proportion of the ethylene oxide explosively decomposed compared with what would be likely to be burnt once the vessel had fractured.

Dr. BURGOYNE said that he had taken the energy to be released from the decomposition of ethylene oxide only. Insofar as combustion of the decomposition products in the surrounding area had contributed to the release of energy responsible for damage, the calculated amount of ethylene oxide involved would be less.