

EXPLOSION HAZARDS IN THE MANUFACTURE OF TEREPHTHALIC ACID

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SUMMARY

The manufacture of terephthalic acid by the oxidation of *p*-xylene with nitric acid involves an explosion hazard. This arises since the gases evolved during the oxidation are capable of supporting the combustion of *p*-xylene. The paper discusses this problem and indicates how the plant has been designed to operate safely.

The operation of the plant could have been safeguarded by the injection of inert gas but considerable quantities of inert gas would have been required and the process would have been costly to operate. Instead, each plant unit has been considered individually and separate safeguards were either incorporated into the design of each unit or into the method of operation. The safety of the oxidation autoclaves is ensured by keeping the partial pressure of the steam high enough to inhibit combustion. The explosion hazard in the condensing system is accepted and the unit is designed to minimise damage if an explosion occurred. Large storage tanks are necessary to enable the recovery of nitric acid to be carried out continuously and safety in these is ensured by keeping the *p*-xylene content below the lower limit of flammability.

An account is given of some of the experimental techniques and apparatus used to obtain basic data for the design and operation of the plant.

Introduction

Terephthalic acid is made in large quantities by Imperial Chemical Industries Limited as an intermediate in the manufacture of Terylene. *p*-Xylene is the raw material and this is oxidised in one stage to terephthalic acid using nitric acid as the oxidising agent at elevated temperatures and pressures. The process involves an explosion hazard and it is proposed to discuss this problem and to describe the apparatus and techniques used to obtain the data required to enable the plant to operate both safely and economically. For obvious reasons it is not possible to describe the plant in detail but the type of plant involved and the method of operation is outlined briefly and in general terms, below.

Outline of the process

A diagrammatic flowsheet of a terephthalic acid plant is given in Fig. 1.

The oxidation is a batchwise one and is carried out in the autoclave, A. *p*-Xylene and nitric acid are introduced into the vessel, steam heating applied and the temperature and pressure brought to the operating conditions. The control parameter is the pressure which is defined by the control valve, C.

The evolved gases, consisting of nitrous oxide, nitric oxide, nitrogen, and carbon dioxide, are passed through the condensing system and condensed material returned to the autoclave. The gases then pass through the pressure control valve and are stored in the buffer tanks, D.

Large buffer tanks receive gas under pressure from a number of autoclaves. The vessels have large capacity and smooth the gas flow from the batchwise oxidations so enabling the recovery of nitric acid to proceed in a continuous manner. They are thus very important; a single autoclave being out of action is not critical but damage to the buffer tanks would close the whole plant.

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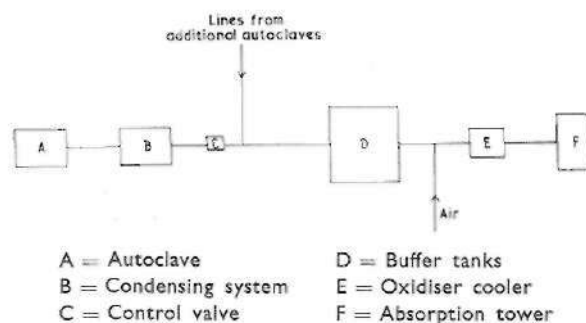


Fig. 1.—Diagrammatic flowsheet of terephthalic acid plant

The gas containing nitric oxide is passed from the buffer tanks to the oxidiser-cooler, E, where, after admixture with air, the nitric oxide is oxidised to nitrogen dioxide. The absorption of nitrogen dioxide to give nitric acid is carried out in the absorption tower, F.

Nature of the explosion hazard

The mixture of nitrogen oxides generated during the oxidation is capable of supporting the combustion of *p*-xylene. There is, therefore, the danger of a vapour-phase explosion in the autoclaves, condensing system, buffer tanks and oxidiser-cooler. In the oxidiser-cooler, however, there is an additional danger. Under certain conditions organic material may separate out as a liquid phase and dissolve nitrogen dioxide to form a potentially explosive liquid. Liquid mixtures of this type constitute the well-known Sprengel-type explosive.

In safeguarding the plant no attempt has been made to track down and eliminate all possible sources of ignition. The approach has been either to operate the plant so that the vapour spaces of the various units are filled with non-flammable gas or, when this is impossible, to design the plant to minimise explosion damage.

It would have been possible to safeguard the plant, with the exception of the oxidiser-cooler, by the injection of inert gas. This would have required the nitrogen content of the evolved gases to be raised to about 60% and would have made the process extremely costly to operate. Instead each plant unit has been considered independently.

Safety in the autoclave is achieved by operating at such a temperature that the amount of steam in the vapour space is sufficient to prevent an explosion. Clearly, it is impossible to operate the condenser under such conditions and the explosion risk in this vessel has been accepted. The vessel has been designed to minimise damage if an explosion occurs and venting devices have been fitted to prevent explosion pressures from being transmitted to the autoclave. The *p*-xylene in the gas passed to the buffer tank is measured and if this exceeds the lower limit of flammability inert gas is injected and the plant is closed down. The oxidiser-cooler is carefully designed to be self-draining to the absorption tower. As an additional safety measure the large plant units, *i.e.* autoclaves, condensers, and buffer tanks, are operated behind blast walls.

The safety precautions taken in the operation of each unit are described in the following sections.

Safety in Individual Plant Items

Autoclave

The problem in connection with the autoclave is to define a safe minimum temperature so that the amount of steam in the vapour is great enough to keep the gas non-flammable. If the temperature falls below this point the batch is stopped and the pressure reduced, so displacing the gas in the autoclave by steam. It is of some importance to define this minimum safe temperature fairly accurately. If it is too low

there is the danger of producing an explosive gas mixture. If it is higher than necessary batches are stopped unnecessarily and production is curtailed and cost increased.

Experimentally, it is somewhat complicated to determine this minimum operating temperature since the process is operated batchwise and conditions in the autoclave change as the oxidation proceeds. The main gaseous products are nitric oxide and nitrous oxide and the proportion of these in the evolved gases alters throughout the oxidation cycle. To limit the work involved and to simplify plant operation, it was necessary to determine which was the most dangerous mixture and then to carry out experimental work with gas of this composition. This was relatively easy since it was found that the limits of flammability of *p*-xylene in nitrous oxide were wider than in nitric oxide. Attention was therefore centred on the gas mixture containing the maximum ratio of nitrous oxide to nitric oxide. It is an added complication that the partial pressure of *p*-xylene in the autoclave changes as the reaction proceeds. Initially, the mixture in the autoclave consists of two liquid phases: (1) dilute nitric acid and (2) *p*-xylene. The gas space above the liquid contains gas saturated with water and *p*-xylene at the temperature of the autoclave. As the reaction proceeds the liquid *p*-xylene disappears and hence the partial pressure of *p*-xylene in the gas phase falls from its equilibrium value at this temperature to a very low value depending on the degree of completion of the reaction. Since the partial pressure of *p*-xylene is not strictly defined it is quite impossible to operate above the upper limit of flammability; safety must, therefore, be based on steam pressure alone.

The safe temperature was determined by measuring the limits of flammability of *p*-xylene in the most dangerous gas and investigating the effect of steam on these limits. The apparatus is shown diagrammatically in Fig. 2. It consists

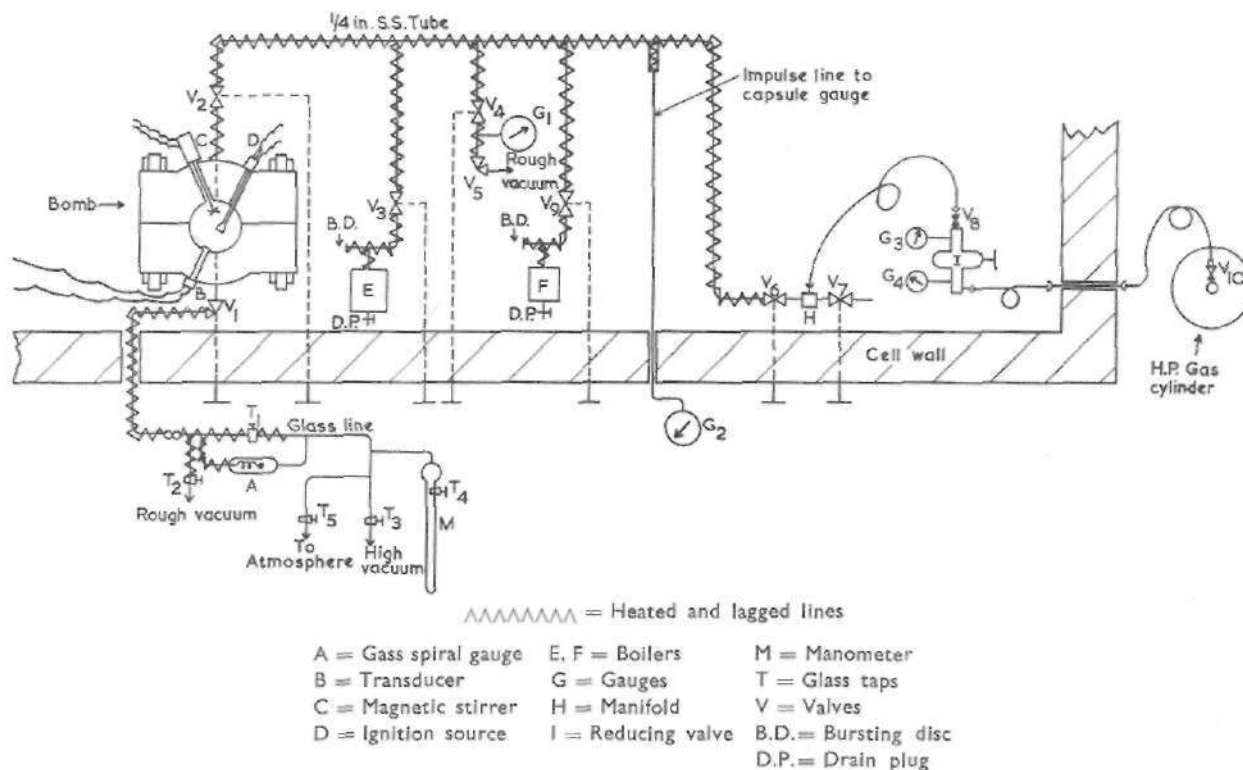


Fig. 2.—High pressure explosion apparatus

of a bomb with a spherical cavity in which gas mixtures are made and tested for flammability. Two bombs are available, one having a capacity of three litres and the other a capacity of six litres. Connected to the bomb are two heated boilers, E and F, which can be used as reservoirs of steam or flammable vapour. The connections in the apparatus are by lens-ring joints and the system will withstand pressures of the order of 3-4000 lb/in² and in addition can be evacuated down to pressures of 10⁻³ mm Hg. The latter condition is necessary since gas mixtures are made up by the method of partial pressures.

Gas mixtures are made up in the bomb by admitting the required vapours at defined pressures and then adding oxidising gas to the required total pressure. Vapour pressures up to about 1.5 atmospheres are measured with a glass spiral gauge, A, used as a null instrument, but above this pressure the capsule Budenburg gauge, G₁, with the capillary impulse line is used. The oxidising gas is then added using the remote controlled operating valves and measuring the pressure by the capsule Budenburg gauge, G₂, outside the cell. The gases in the bomb are thoroughly mixed by the totally-enclosed magnetic stirrer, C, and then tested for flammability by fusing a wire positioned in the centre of the spherical cavity. The rise in pressure is used as the criterion of flammability. This is measured by the transducer, B, the signals from which are amplified and then displayed on a cathode-ray oscilloscope; the transducers used are either diaphragm or strain-gauge type instruments. The ignition source was chosen after experiments with hot wires and high tension sparks had shown that the measured limits of flammability were independent of the type of ignition source. The flammability determinations were carried out at the autoclave operating pressure and at a fixed temperature near to the expected minimum safe temperature. The precise temperature is unimportant provided it is sufficiently high to keep the steam and *p*-xylene in the vapour phase. The results are shown diagrammatically in Fig. 3. The apices of the triangle represent steam, *p*-xylene vapour, and reaction gas under the given conditions, and the area within the triangle therefore

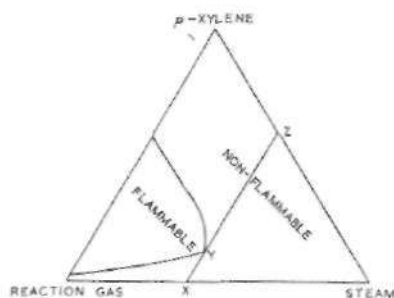


Fig. 3.—Diagrammatic representation of limits of flammability for autoclave gases

represents mixtures of these compounds.' The safe operating conditions are represented by the area to the right of the line X-Y-Z. This line represents the minimum steam partial pressure required to suppress the combustion of *p*-xylene in reaction gas. The temperature at which the water vapour pressure becomes equal to this pressure is the minimum safe temperature of autoclave operation.

Condenser

As the gas from the autoclave passes through the condenser, steam and *p*-xylene are stripped out and the gas mixture passes through the flammable region. The approach has been to accept this and to build the plant to minimise damage if an explosion occurs rather than to render the gas non-flammable by the injection of inert gas. It is also believed that any potential source of ignition would be in the hot autoclave and not in the relatively cool condenser. Since the autoclave is operated under non-flammable conditions this adds a further margin of safety.

The condensers have been made to withstand the maximum computed explosion pressures. These pressures, calculated according to simple thermochemical principles neglecting the dissociation of combustion products and cooling, are in the region of 3000 lb/in². To prevent dangerous pressures from being transmitted to the autoclaves, bursting discs have been fitted to the condenser and to the autoclave. Since right-angle bends occur at each end of the condenser, bursting discs have been placed at each corner in line with the condenser tubing. It is considered that bursting discs in these positions would be very efficient but no experimental work has been carried out to prove this. Assuming an instantaneous rise in pressure to 3000 lb/in² in the condenser it has been calculated that these discs would prevent the pressure in the autoclave rising above the test pressure.

In calculating the explosion pressures it has been assumed that hydrodynamic effects in the combustion process were absent. No attempts have been made to determine the ability of these gas mixtures to propagate a detonation wave. If a detonation wave were propagated the pressures in the Chapman-Jouguet zone would be about 6000 lb/in². Approximate calculations have been made taking into account the very short times during which these pressures would be exerted and these show that the condenser would probably withstand these pressures. The very high pressures frequently observed prior to the initiation of a stable detonation wave would probably damage this plant unit but it would be quite uneconomic to attempt to guard against this.

To prevent injury to personnel each autoclave and condensing system is isolated in a separate blast cubicle.

Buffer tanks

The gas from the autoclaves is stored in the buffer tanks at elevated pressures and ambient temperatures. The gas contains nitric oxide and nitrogen oxide in the ratio of NO : N₂O = 2:1 with about 20% by volume of inert gas (carbon dioxide and nitrogen). Since the tanks are operated continuously, the gas composition remains sensibly constant.

The limits of flammability of *p*-xylene in this mixture of nitrogen oxides and the effect of nitrogen on these limits have been investigated at atmospheric pressure and higher pressures to cover the operating conditions of the tanks. The experiments under pressure were carried out using the spherical bomb described above; the limits at atmospheric pressure were determined using the apparatus shown diagrammatically in Fig. 4. A flow technique is used to obtain mixtures of fuel and oxidising gas of known composition. Synthetic gas mixtures contained in the cylinder A are passed through a saturator, F, G, containing the fuel and saturated with the vapour of the fuel at a definite temperature. The saturator consists essentially of a high temperature bath, F, situated inside a low temperature bath, G; the low temperature bath is maintained accurately at a given temperature whilst the high temperature bath is kept about 15°C hotter.

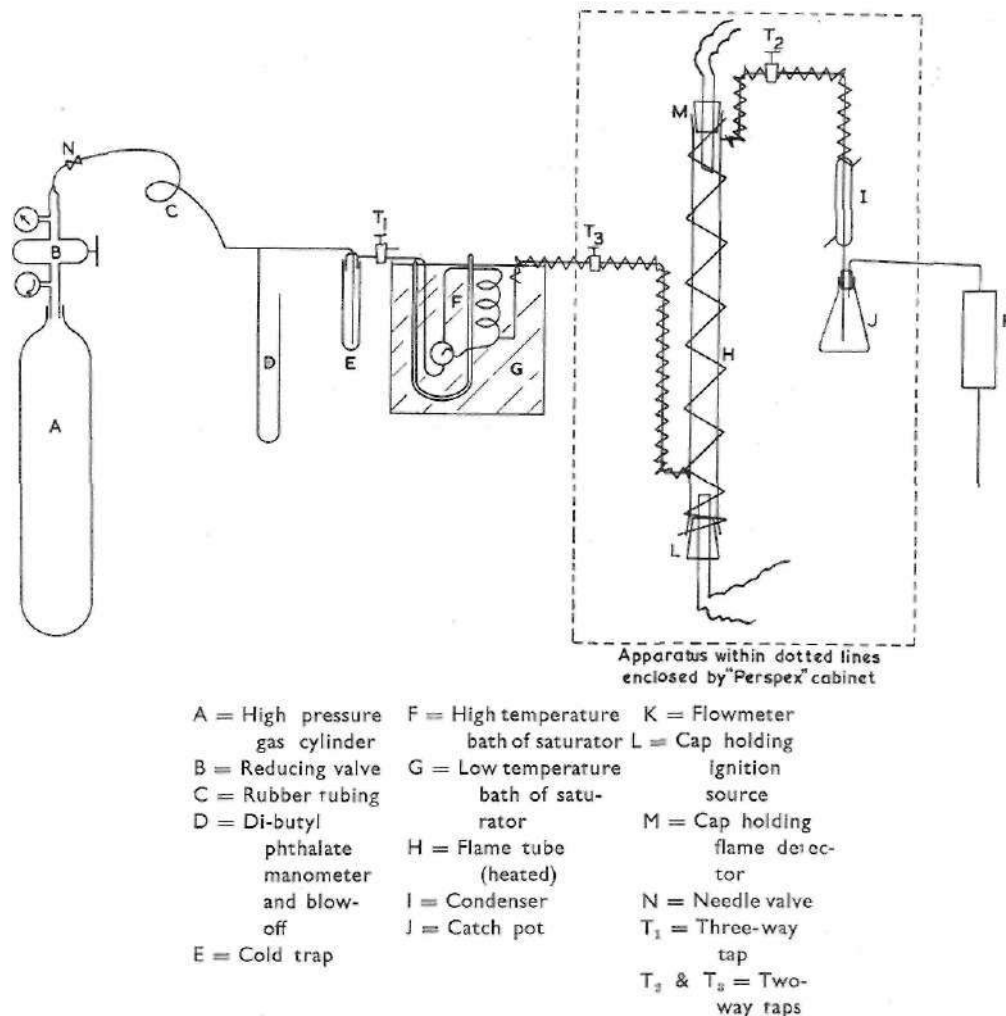


Fig. 4.—Schematic diagram of atmospheric pressure explosion apparatus

The gas is bubbled through a vessel containing fuel in the high temperature bath and then passed through a cooling coil in the low temperature bath. In principle, therefore, the gas is "over-saturated" with fuel vapour in the bath, F, and then brought to equilibrium saturation with vapour at the temperature of the bath, G.

In this way a gas stream can be accurately saturated with vapour at flow rates of about a litre per minute. The mixture of gas and vapour is then passed to the long tubular vessel, H, where it is tested for flammability. If saturation is carried out at a temperature higher than ambient then the lines from the saturator and the tube H are heated to prevent condensation. The tube H is a glass tube 4 ft long and 2 in. internal diameter. It is surrounded by a slightly wider tube serving as a former for the electric heating wires and by an additional thick-walled "Visible Flow" tube acting as a thermal shield and as a protection against flying glass in the event of the rupture of the flame tube. A flammability determination is made by closing the taps T₃ and T₂, withdrawing the cap L and then attempting ignition using the source L which may be a high-tension spark or a hot wire. The criterion of flammability is the distance a flame travels up the flame tube after attempted ignition, the limit composition being taken as that mixture in which a flame is propagated just short of the full length of the tube. The

ignition source was obviously more than adequate since near the limits flames could be initiated which only travelled part of the way up the tube. Some flames are difficult to detect visually but additional help is given by the flame detector, M, which consists of a thermocouple or thermistor.

To determine the amount of nitrogen required to inhibit the combustion of *p*-xylene in these gases the experiments were carried out at 100°C. in order to provide sufficient *p*-xylene in the vapour phase. The results at atmospheric pressure are shown in Fig. 5; increasing pressure widens the limits.

Under normal operating conditions the content of *p*-xylene of the gas from the autoclaves is quite well removed from the lower limit of flammability. Certain abnormal operating conditions, e.g. an overloaded condensing system, could, however, increase the content of *p*-xylene above the lower flammability limit. If the content of *p*-xylene reaches about half the lower limit value inert gas is injected and the plant closed down for investigation.

The method of measuring the content of *p*-xylene is novel and perhaps of interest. Since the gas contains small amounts of nitrogen dioxide infra-red and ultra-violet techniques cannot be used. A bleed of gas is taken from the manifold leading to the buffer tanks and the pressure reduced to atmospheric pressure in order to evaporate any mist that might be

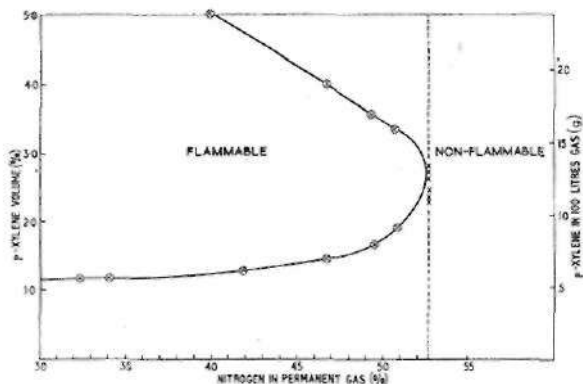


Fig. 5.—Effect of nitrogen on limits of flammability of *p*-xylene in a mixture of nitric oxide and nitrous oxide (NO : N₂O = 2 : 1) at atmospheric pressure.

present. The gas is then passed through a bed of catalyst and the *p*-xylene oxidised to carbon dioxide and water. The rise in temperature of the bed is a measure of the *p*-xylene concentration. The instrument is, of course, fitted with flame traps to prevent "flash-back".

Eventually, it is hoped that the *p*-xylene monitor will automatically inject gas when the *p*-xylene reaches a dangerous level. Inert gas would then be injected to make the gas entering the buffer tank non-inflammable and also to ensure that the gas mixture remained non-inflammable after admixture with the buffer tank contents.

Oxidiser-cooler

The gas from the buffer tanks is mixed with about four times its volume of air and passed to a long water-cooled tube called the oxidiser-cooler where exothermic reaction occurs to give nitrogen dioxide.

The amount of *p*-xylene vapour present is below the lower limit of flammability and hence under normal conditions there is no danger of a gas-phase explosion. However, it has been found that chemical reaction occurs between the *p*-xylene vapour contained in the gas from the buffer tanks and the nitrogen oxides to give the less volatile nitrated compounds. On cooling the gas these nitro-compounds separate out as a liquid phase and dissolve nitrogen dioxide, forming a liquid mixture which has been shown to be capable of detonation. To minimise the hazard the coiled pipes of the oxidiser-cooler and the gas line leading to the absorption tower have been carefully positioned so that the complete system is self-draining to the absorption tower. Liquid cannot accumulate in the system in any significant quantity. It has also been shown that the thin film of liquid in the pipe is not sufficient to rupture it in the event of detonation occurring. The nitro-xylenes are also sufficiently soluble in the strong acid at the base of the tower to be removed in solution in the recovered acid. The potential hazard has, therefore, been reduced to a minimum.

Conclusions

The work done on explosion hazards has enabled changes to be made in the terephthalic acid plant, which cannot be detailed here, but which have increased safety without affecting economic production. It is hoped that this review will be of value in assisting others to attack similar problems.

Acknowledgment

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