

FLAMMABILITY ASPECTS OF THE MANUFACTURE OF PHTHALIC ANHYDRIDE

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The flammability limits of phthalic anhydride and naphthalene in air and oxygen depleted atmospheres have been determined at temperatures of 250-<sup>o</sup>C. Some measurements have also been made on the suppressant effects of catalyst dust on the flammability of phthalic anhydride/oxygen/nitrogen mixtures. The application of the experimental results to the manufacture of phthalic anhydride by the oxidation of naphthalene and o-xylene in fixed and fluid catalyst beds is considered.

INTRODUCTION

Phthalic anhydride is manufactured by the air oxidation of naphthalene in a fluidised bed of catalyst. It can also be produced by the oxidation of either naphthalene or o-xylene in a fixed catalyst bed.

The fluid bed process consists of a dense bed of a finely powdered support, usually silica, which has been impregnated with vanadium pentoxide and a suitable moderator. Above the fluidised catalyst bed there is normally a large disengaging space surmounted by filters designed to prevent the escape of fine catalyst particles from the converter to the condensing sections of the plant.

In the fixed bed process the catalyst is usually pelleted vanadium pentoxide packed into a number of narrow vertical tubes mounted in a converter with a heat transfer medium circulating between them.

In both processes air/naphthalene or o-xylene mixtures are fed into the catalyst bed, which has been preheated to 300-<sup>t</sup>00<sup>o</sup>C, and the large heat evolution from the oxidation reaction serves to maintain the plant gases in this temperature range. After passing through the catalyst bed the phthalic anhydride produced is condensed to a liquid or a solid.

The plant vessels could, therefore, contain flammable mixtures of naphthalene, o-xylene or phthalic anhydride vapours with air at high temperatures. The presence of sources of ignition such as hot surfaces (above the autoignition temperatures of the organic materials) is likely and pyrophoric deposits also cannot be excluded from the plant.

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The most hazardous plant sections are the feed sections, which will contain air/naphthalene mixtures and the sections after the catalyst bed, where mixtures of phthalic anhydride vapour and oxygen containing gases will be present. Once the air/naphthalene mixture has entered the dense catalyst bed (fixed or fluid) no flame propagation can occur due to the suppressant effects of the catalyst itself.

Safe operation of a phthalic anhydride plant requires, therefore, accurate data on the flammability limits of the product and also of the starting materials, naphthalene and o-xylene.

Some literature data Schwab and Doyle (1), U.S. Bureau of Mines (2) and (3) exists on the flammability limits of naphthalene and phthalic anhydride in air at moderate temperatures and there is also a little data on the flammability of o-xylene (3). Since a phthalic anhydride plant operates at temperatures in the 300-400°C range and mixtures of oxidation products and gases containing less oxygen than normal air are produced, much more comprehensive flammability data obtained at temperatures up to 400°C is required. This paper deals with the experimental determination of these limits and discusses their application to phthalic anhydride manufacture.

Another feature of the fluid bed manufacture of phthalic, the flame suppressant properties of catalyst particles in the plant disengaging space, is also discussed and data on the magnitude of this effect presented.

#### EXPERIMENTAL

##### 1. Flammability Limits of Phthalic Anhydride

The measurements were carried out in the apparatus shown in Fig.(1).

This consisted of an ignition chamber, a vertical glass tube 5-1 cms (2 ins) in diameter and 1.22 m (4 ft) long, which was heated electrically to temperatures up to 400°C. The gas mixtures were prepared by passing oxygen/nitrogen mixtures of known composition in a spiral path through molten phthalic anhydride contained in a saturator. The temperature of the saturator was controlled to produce phthalic anhydride/oxygen/nitrogen mixtures with the desired composition and the actual composition checked by burning a portion of the mixture in a furnace packed with combustion catalyst and analysing the gases produced. At the high temperatures (300-400°C) of the experiments slow oxidation of phthalic anhydride or naphthalene occurs on the walls of the glass combustion chamber under static conditions. The gas mixtures to be tested were, therefore, passed through the tube until steady conditions were attained, the gas flow stopped and an immediate attempt made to ignite the mixture at the base of the tube. Ignition was judged to have occurred if a flame propagated away from the electrodes.

By varying (a) the temperature of the ignition chamber, (b) the composition of the oxygen/nitrogen supporting atmosphere, (c) the partial pressure of the phthalic anhydride (or naphthalene) vapour in the supporting atmosphere, the flammability limit data shown in Figs. (2) and (3) were produced.

##### 2. Effects of Catalyst Dust on Flammability Limits

These measurements were carried out using catalyst with a particle size below 76 microns, which had been recovered from the disengaging space of a

full scale fluid bed plant. The powder was dispersed by a vibratory feed hopper into a fast flowing phthalic anhydride/oxygen/nitrogen mixture and the gas mixture containing the entrained catalyst was fed into the top of the ignition chamber. The gas flow was stopped momentarily and the mixture ignited at the bottom of the tube. The actual catalyst concentration for each experiment was calculated from the known volume of the tube and the weight of catalyst collected at its base.

The results of these experiments are shown in Figs, (k) and (5). Experiments of this nature are obviously difficult and time consuming and measurements were made at only one temperature,  $400^{\circ}\text{C}$  and for a supporting atmosphere containing  $\sim 14\%$  by vol. oxygen (86% nitrogen) to give an assessment of the flame quenching properties of catalyst dust.

Previous workers in this field, Dolan and Dempster (4), found that the quenching efficiency of a powder was proportional to its surface area, but they worked with powders where the true surface area and geometric surface area, determined from particle size, were close to one another. In the present work the catalyst surface area (by argon adsorption) was large (approximately 100  $\text{m}^2/\text{g}$ ) compared to the geometric surface area. Figs, (k) and (5) show that catalyst dust is an effective flame suppressant and that the geometric surface area is the critical factor in flame suppression.

#### APPLICATION OF EXPERIMENTAL DATA TO PLANT OPERATION

##### A. Fluid Bed Plants

In the case of the fluid bed reactor the naphthalene feed is led into the catalyst bed as a liquid together with some "primary air", while most of the air used in the oxidation is fed in below the naphthalene injection points as so called carrier air, which is used to fluidise the catalyst.

A.1. Application of Flammability Limit Data. The primary air under normal running conditions gives a mixture with naphthalene, which is above the upper flammability limit (Fig. (2)). Blockage of the naphthalene feed with no corresponding change in the air flow would, however, create flammable conditions. The primary air for this feed system should, therefore, be diluted with nitrogen to give an oxygen concentration below the limiting oxygen content to support combustion. Examination of Fig. (2) shows that this is  $8\%$  by volume of oxygen at  $350^{\circ}\text{C}$ .

Once inside the dense bed the thermal capacity of the catalyst is sufficient to prevent any spread of flame in the reaction mixture during the oxidation process. It is only when the products of reaction and supporting atmosphere leave the dense bed and enter the catalyst disengaging space that the flammability aspects of the gas phase must again be considered.

The reactant gas stream is depleted in oxygen by the oxidation processes. The extent of the depletion is dependent on the initial naphthalene concentration in the gaseous mixture and on the extent of the two main oxidation processes, which occur, viz:

1. Conversion of naphthalene to phthalic anhydride.
2. Complete oxidation to carbon dioxide and water.

With this in mind, "operating lines" for various conversions of naphthalene to phthalic anhydride were superimposed on the flammability curves in

Fig. (3). In each case it was assumed that naphthalene not oxidised to phthalic was converted to carbon dioxide and water. These curves show the supporting atmosphere to phthalic anhydride weight ratio plotted against the oxygen content of the supporting atmosphere for a range of conversions of naphthalene to phthalic, and they represent the only possible gas mixture compositions after naphthalene oxidation, with the assumptions made.

Plant operating data indicate that the operating line representing 90% conversion to phthalic anhydride is most applicable to conditions existing during normal production. Examination of Fig. (3) shows that the 90% conversion line enters the 400°C flammable zone at a supporting atmosphere to phthalic anhydride weight ratio of 22.6:1 (0.86 mol % phthalic anhydride). This mixture would be produced from an air/naphthalene feed mixture with a 23.5:1 weight ratio (0.97 mol % naphthalene), which is, therefore, the limiting safe feed composition at 400°C without alteration of the operating procedure. Further consideration of the 90% conversion line in Fig. (3) shows that it emerges from the 400°C flammability zone at a weight ratio of 9.0:1 (2.1 mol %) supporting atmosphere to phthalic anhydride, which corresponds to a pre-reaction air to naphthalene weight ratio of 9-3:1 (2.42 mol %). Once this feed rate or greater is attained non-flammable conditions exist. Modification of the process is, therefore, necessary to make the transition from the safe side of the lower flammability limit to the safe side of the upper limit. This transition is best accomplished by the addition of nitrogen to the main fluidisation or carrier air. In addition the air used to blowback the filters at the top of the reactor (to prevent their blockage with catalyst fines) must also be diluted with nitrogen, since this blowback air enters the reactor and has a significant effect on the composition of the disengaging space gases.

The operation is shown diagrammatically in Fig. (6). Feed gas of composition a, (modified to aa by blowback gases) is altered in composition to b (bb with blowback gases) by substitution of nitrogen for part of the main air stream. At this stage the naphthalene content of the feed is increased so that the new composition is represented by c (cc with blowback) and further increase in naphthalene content gives a composition of d (dd with blowback). At this stage the nitrogen flow is reduced at the same time as the naphthalene feed is increased, until finally e (ee) is reached and the nitrogen in the main air stream is zero.

The whole operation is controlled automatically and the reverse procedure is followed in the event of a shut down. During normal operation the oxygen content of the gases leaving the converter is monitored continuously and checked at frequent intervals by independent gas analysis to ensure that it is below the critical level for supporting combustion. Any deviation from normal running procedure automatically cuts off the naphthalene feed and introduces nitrogen into the main flow. Similarly the transition sequence cannot be initiated if the nitrogen supplies are inadequate, and if they fail during the transition the naphthalene feed is cut off.

One factor not considered above is the effect of pressure. Most fluid bed plants operate under a pressure of about 2 bar.g. Literature data, U.S. Bureau of Mines (3), shows, however, that the effect of pressure, especially pressures of this low order, on flammability limits is negligible.

A.2. Flame Suppressant Effect of Catalyst Dust. The disengaging space between the top of the dense catalyst bed and the filters at the top of the converter is usually of wider diameter and, because of its large volume and high temperature, constitutes the most dangerous section of the plant.

The measurements on the suppressant effects of catalyst dust Fig. (k) show that a catalyst density of 0.055-0.07 lb/ft<sup>3</sup> (0.88-1.12 gm/l) in the disengaging space provides safety down to a 12:1 supporting atmosphere to phthalic anhydride weight ratio (equivalent to 1.6 mol % phthalic anhydride), where the supporting atmosphere contains ~4% oxygen. The equivalent value in terms of surface area is 3.2-<sup>1</sup>m<sup>2</sup>/ft<sup>2</sup> (0.113-0.1<sup>5</sup>m<sup>2</sup>/l). The geometric area of the catalyst used in these experiments was 0.13 sq.metres/gm.

Optimisation of plant operating conditions in terms of yield and purity of product usually produces conditions such that the catalyst density and surface area/volume ratio in the disengaging space are far greater than the figures quoted above for a 12:1 weight ratio of supporting atmosphere to phthalic anhydride.

Safe operating conditions can be achieved in the disengaging space by control of the naphthalene feed mixture, composition of the carrier gas, etc., as described above. However, the presence of fine particles of catalyst dust does provide an extra measure of safety in this hazardous section of the plant.

The dust cannot protect the parts of the plant beyond the catalyst filters, but here the temperature is lower and the vessel volumes are smaller and safety can readily be achieved by control of the oxygen content of the supporting atmosphere.

#### B. Fixed Bed Plants

Fixed bed phthalic anhydride plants operate either on a feed of naphthalene as for fluid bed plants or use o-xylene as the feed material. Again, as in fluid bed manufacture, the concentration of phthalic anhydride in the gases leaving the converter should be kept below the lower flammability limit.

Fixed bed oxidation of air/naphthalene mixtures usually gives a conversion to phthalic of not greater than 8C\$. Reference to the 80\$ conversion line in Fig. (3) shows that the product gases are flammable for a supporting atmosphere to phthalic anhydride weight ratio of less than 22.5:1 (0.86 mol % phthalic). This is equivalent to an air/naphthalene feed ratio of 20.5:1 (1.1 mol % naphthalene). Oxidation of o-xylene to phthalic anhydride gives a maximum conversion to the product of about 60%. Examination of Fig. (7) shows that the 6C\$ conversion line enters the 400°C flammability limits at 21.5:1 weight ratio of supporting atmosphere to phthalic anhydride (0.90 mol %). This produce mixture is produced by an initial air/o-xylene feed of 17-9:1 (1.50 mol %).

A few measurements were made of the flammability limits of o-xylene in air, and Table (1) shows the results of these measurements together with corresponding figures for naphthalene and some limit data obtained by extrapolating the experimental measurements to lower temperatures.

TABLE 1 - Flammability Limits of Naphthalene and o-Xylene

Temperature (°C)	Flammability Limit (Weight Ratio of Air to:)			
	Naphthalene		o-Xylene	
	Lower Limit	Upper Limit	Lower Limit	Upper Limit
MDO			37.0:1	
350	35-^:1	2.2:1		
300			33.0:1	
250	30.5:1	2.5:1		
200	28.5:1*		30.0:1	5.5:1
150	26.7:1*		28.5:1	3.75:1

\* = Extrapolated Result.

Examination of this table shows that even if it is practicable to make the exit gases from the catalyst beds non-flammable by operating with weight ratios of greater than 20.5=1 for naphthalene and 17-5 for an o-xylene feed, the feed mixture will still be flammable. In any case production reasons usually dictate that feed mixtures appreciably richer in naphthalene or o-xylene than the above must be used.

As in fluid bed plant operation using a carrier gas containing less oxygen than normal air could overcome this flammability problem. However, fixed bed converters are smaller and more mechanically robust that the large reactor required for efficient fluid bed operation. This means that explosion venting can be employed to protect the converter against the effects of an explosion due to operating inside the flammability limits.

Explosion pressure measurements on mixtures of air with phthalic anhydride, naphthalene and o-xylene vapours in small closed vessels showed that the maximum possible explosion pressure for any mixture, initially under atmospheric pressure, is about 8 bar.g. (120 psig). Reduction in the oxygen content of the supporting atmosphere reduced both the maximum explosion pressure and rates of pressure rise appreciably. Increase in the initial temperature of the flammable mixture also reduced the maximum explosion pressure.

Precise design of explosion vents for a fixed bed converter from explosion pressure measurements carried out in a small vessel is not possible, however, due to the effect of turbulence. The rate of pressure rise in an explosion increases rapidly with increase in the degree of turbulence of the mixture and no correlation is possible between degree of turbulence produced in a small test vessel and that present in the full scale plant.

Protection can be provided for a fixed bed plant, however, by making the converter as strong as possible and fitting explosion vents with areas as close as possible to the cross-sectional area of the converter itself. The section of the converter before the catalyst bed contains mixtures of naphtha-

lene or o-xylene with air while the regions of the plant downstream from the catalyst bed contain gases with less oxygen than normal air. Larger vents should, therefore, be fitted to the converter inlet than to its outlet.

#### CONCLUSIONS

The available flammability limit data can be used to define safe operating conditions for fluidised bed phthalic anhydride plants.

Safe operation of fixed bed units under conditions of maximum phthalic anhydride production is less certain. The provision of large explosion vents, the use of a mechanically strong converter and elimination of obvious sources of ignition will give a reasonable measure of safe operation.

#### REFERENCES

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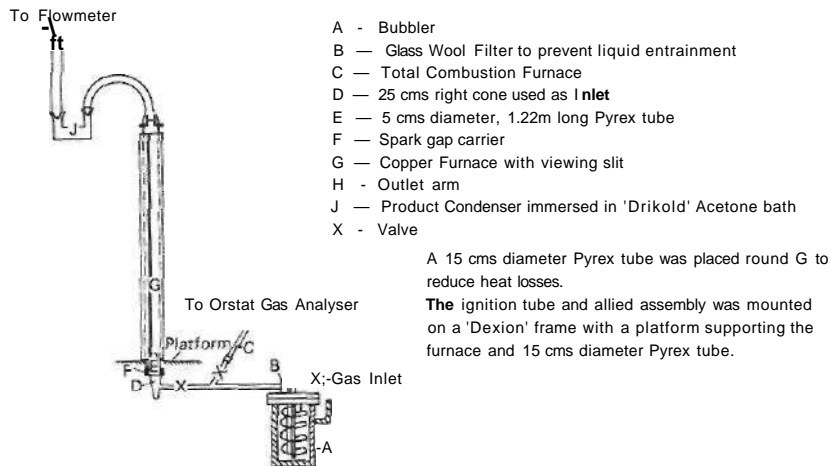


FIG (1):- FLAMMABILITY LIMIT APPARATUS

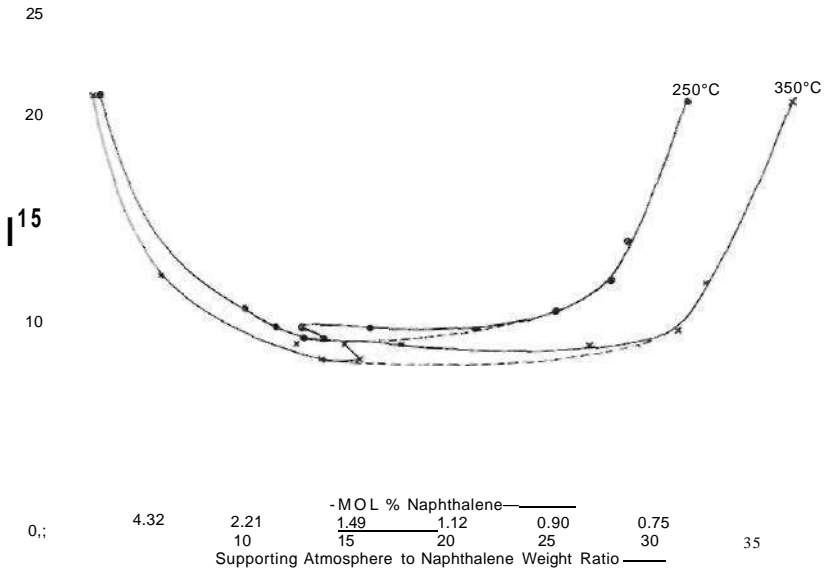


FIG (2):- FLAMMABILITY LIMITS NAPHTHALENE - OXYGEN - NITROGEN MIXTURES



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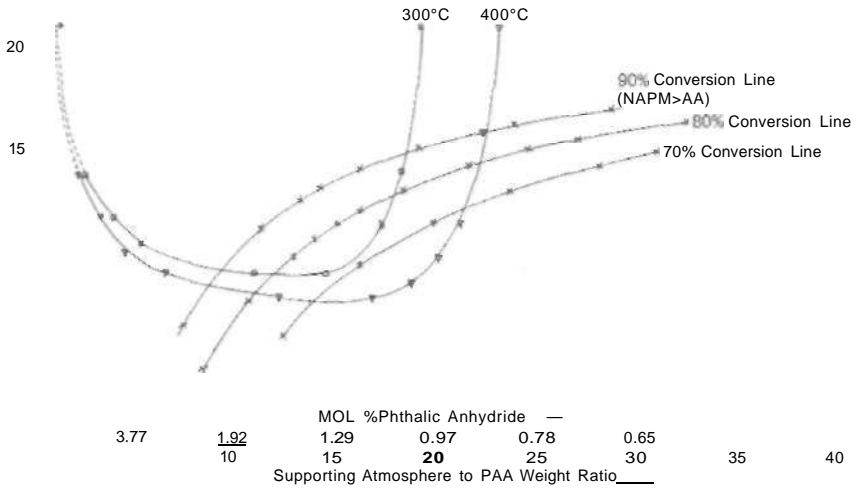


FIG ( J ):- FLAMMABILITY LIMITS PHTHALIC ANHYDRIDE - OXYGEN - NITROGEN MIXTURES

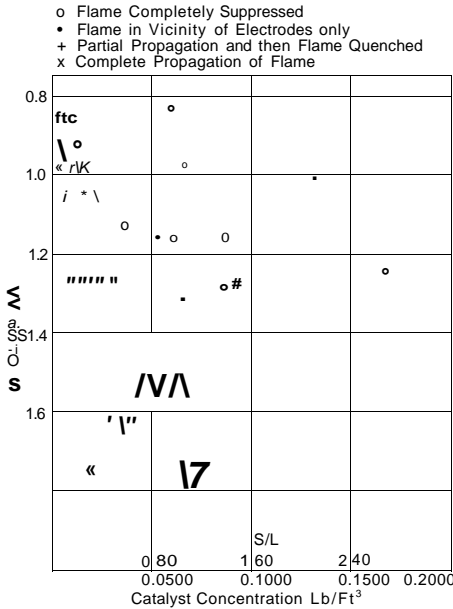


FIG (4):- CATALYST QUENCHING:- EFFECT OF CATALYST CONCENTRATION

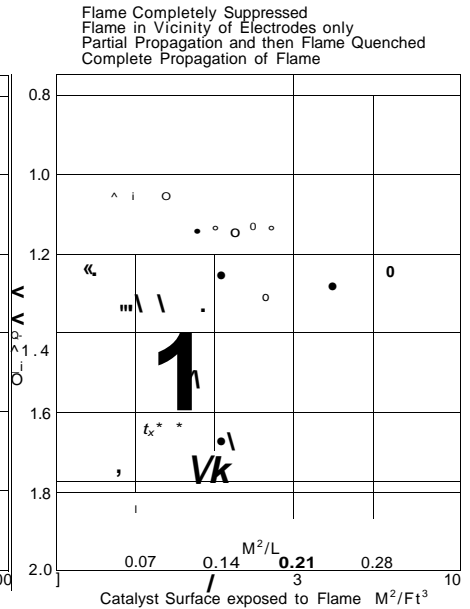


FIG (5):- CATALYST QUENCHING:- EFFECT OF CATALYST SURFACE AREA

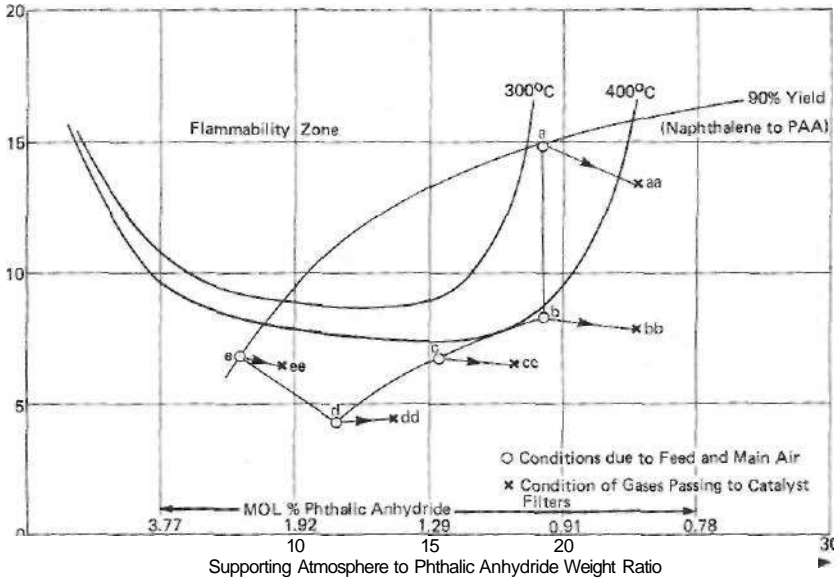


FIG (6):- TRANSITION ROUND FLAMMABLE ZONE

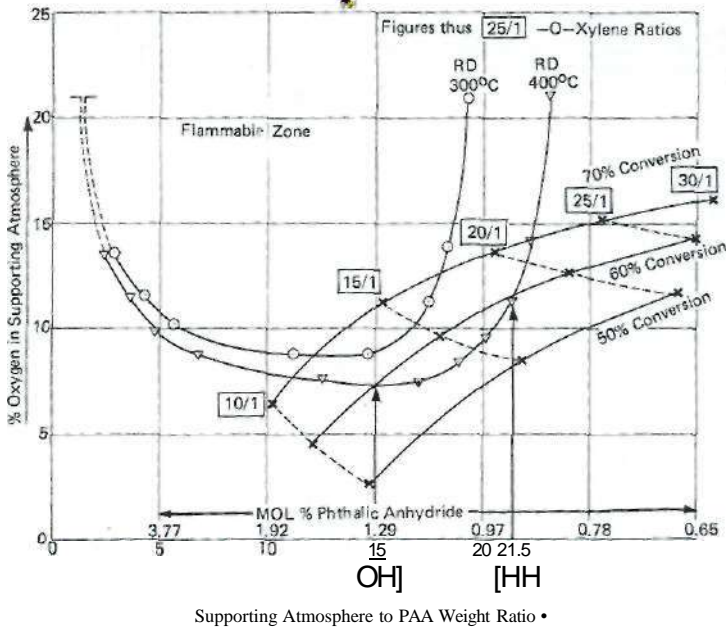


FIG (7):- FIAMMABILITY LIMITS PHTHALIC ANHYDRIDE, O-XYLENE CONVERSION LINES