

# **Effects of Initial Pressure on the Flammability Limit of OX-Air Mixture with 20-L-Appartus**

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## **Abstract**

Knowledge of material safety properties is essential for the safe handling of unit operations. Incidents in plants can often be traced to an insufficient knowledge of the hazardous properties of combustible or flammable substances. If determined carefully and applied properly, safety-related properties could provide information on the reaction behaviors of the specific substance and possible fire and explosion hazards. The aim of this study is to investigate the safety-related properties of o-Xylene (e.g., flammability limits, minimum oxygen concentration, maximum explosion overpressure, flammability zone), which were determined at a mixing operation temperature of 150°C and under initial pressures of 760 mmHg, 1,520 mmHg, and 2,280 mmHg, respectively. Results of an empirical equation for the effects of initial pressure on flammability limit, is established from this study. Potential hazards of unit processes in phthalic anhydride plants are also mentioned.

Keywords: o-Xylene; Flammability limits; Maximum explosion overpressure;

Flammability zone; Phthalic anhydride

## 1. Introduction

Until World War II, phthalic acid (PAC) and, later, phthalic anhydride (PA), were manufactured primarily by liquid-phase oxidation of a suitable feedstock. The favored method was BASF's oxidation of naphthalene by sulfuric acid in the presence of mercury salts to form the anhydride. This process was patented as early as in 1896. During World War I, a process to make phthalic anhydride by the oxidation of naphthalene in the vapor phase over a vanadium and molybdenum oxide catalyst was developed in the United States, with U.S. patents being individually granted in 1930 and 1934. Essentially, the same process was developed independently in Germany.

For the safe handling of combustible or flammable substances, it is imperative to understand their dangerous properties. Knowing flammability limits and related information is crucial in the process industries where serious hazards may be encountered within the flammability limits. A fire or an explosion might occur if a flame, hot surface or hot particles are encountered. Currently, the worldwide commercial process for the production of PA is by air oxidation of *o*-Xylene (OX). For a typical loading of 60 g-OX/normal cubic meter of air, the volume concentration of OX would be 1.2 vol.% or 4.5 wt.% of the feed mixture (Park & Sheehan, 1996; Schwab, 1991).

In the USA, Bureau of Mines Bulletin No. 627 reported a lower explosion limit of 1.1 vol.% and an upper explosion limit of 6.4 vol.% of OX, both at 100°C, and an auto-ignition temperature of 465°C (Schwab & Doyle, 1970; Lewis, 1996). However, the prevention of explosion hazards requires other material safety properties.

The study of OX safety properties has particular significance for Taiwan. If the following five projects shown in Table 1 are carried out as planned, Taiwan will become the second largest PA production area in the world, behind only the USA. Various types of incidents with numerous causes have occurred in PA production plants. This study is directed toward the PA process at the entrance of the OX reactor, to estimate potential hazards in advance of completion of the Taiwan projects. However, the results should also provide valuable information for existing process plants.

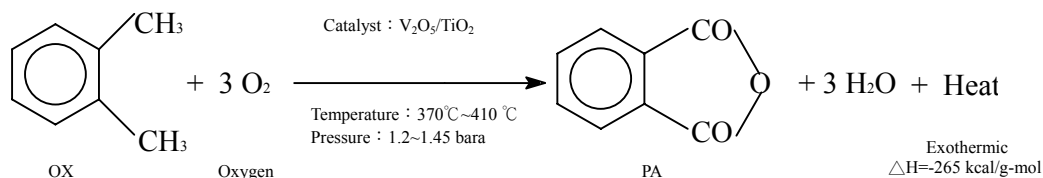
The purposes of this study are to (1) investigate the explosion characteristics of OX as the OX/air mixture enters the reactor, including LEL, UEL, maximum explosion overpressure ( $P_{max}$ ), rate of maximum explosion pressure rise ( $(dp/dt)_{max}$ ), Gas or vapor deflagration index ( $K_g$ ), minimum oxygen concentration (MOC), all at 150°C and between 760 mmHg and 2,280 mmHg (Park & Sheehan, 1996; Schwab & Doyle, 1970; Lewis, 1996); (2) identify the hazards in the PA oxidation process; (3) evaluate the hazards of enhancing the oxygen concentration (21 vol.%, 30 vol.%, and 40 vol.%) in the mixtures, and (4) propose an empirical equation used for increase of initial

pressure.

## 2. Reaction Chemistry and Processes

### 2.1. Chemistry

PA can be produced from OX by catalytic oxidation with air by the following reaction (Park & Sheehan, 1996; Lewis, 1996; Chem. Systems Inc., 1995):



### 2.2. Reaction Processes

The manufacturing process has two major steps: (1) oxidation, which produces the crude PA and (2) finishing, which refines the crude PA to a water-white molten product of at least 99.8 mol% purity (Park & Sheehan, 1996; Schwab, 1991; Chem. Systems Inc., 1995; Graham, 1970).

The oxidation step begins with OX being pumped into an evaporator where it is mixed with the proper amount of preheated air. The feedstock evaporates and forms a gaseous mixture with air at  $150^\circ C$  in the desired proportions before entering the reactor.

The gas stream, containing about 80 gm of OX per normal cubic meter ( $Nm^3$ ) of air, enters the reactor. The air rate is typically  $4 Nm^3$  of air per hour for each catalyst tube which has an inside diameter of about one inch. The reactor is a multi-tube isothermal reactor with catalyst in the tubes. Molten salt circulation across the tube bundles is used to remove the reaction heat. Heat removed in the salt cooler is normally utilized for steam generation. The generation and use of steam is one of the major economic factors in the production of PA (Davies, 1979).

The reactor effluent is cooled by generating steam or by preheating the air to the reactor. The cooled reaction gases are, in turn, sent to switch condensers where crude PA is collected as solid and then melted. The bulk of the PA production is recovered by desublimation, because the dew point of PA is below its melting point ( $131^\circ C$ ). A water jacket serves to dissipate the heat of explosions or to maintain the thermostatically controlled test temperature.

In practice, the process is operated below  $131^\circ C$ . The crude PA from the condensers is about 98 mol% purity, with PAC being the major impurity.

Generally, there are three steps in the finishing stage. The first step is a thermal

treatment to convert (decompose) the remaining PAC to PA. A few of the remaining impurities are maleic anhydride, benzoic acid and phthalide, to name a few.

After the PAC is decomposed in the crude, the second step involves removal of the light ends, commonly by distillation. Similarly, the third step is the separation of higher boiling materials, which are sequentially routed to the second distillation tower. The residues from the towers are usually incinerated (Park & Sheehan, 1996; Schwab, 1991).

### 3. Experimental Apparatus and Procedures

The experimental 20-L-Apparatus (or 20 Liter Spherical Explosion Vessel) was obtained from Adolf Kühner AG and is shown in Fig. 1. The test chamber is a stainless steel hollow sphere with a personal computer interface. The top of the cover contains holes for the lead wires to the ignition system. The opening provides for ignition by a condenser discharging with an auxiliary spark gap (Siwek, 1996; Operating Instructions for the 20-L-Apparatus, 1996), which is controlled by the KSEP 310 unit of the 20-L-Apparatus. The KSEP 332 unit uses piezoelectric pressure sensors to measure the pressure as function of time (ASTM, 1991; Operating Instructions for the 20-L-Apparatus, 1996). A comprehensive software package KSEP 5.0 is available, which allows safe operation of the test equipment and an optimum evaluation of the explosion test results.

In the past, the international standards have described the 1 m<sup>3</sup> vessel as the standard test apparatus (Chem. Systems Inc., 1995). In recent years, increased use has been made of the more convenient and less expensive 20-L-Apparatus as the standard equipment. The explosion behavior of combustible materials (combustible dusts, flammable gases, or solvent vapors) must be investigated in accordance with internationally recognized test procedures. For the determination of combustible gases or vapors, the test is generally accomplished in a quiescent state (ignition delay time,  $t_v = 0$  sec) (Operating Instructions for the 20-L-Apparatus, 1996).

In the 20-L-Apparatus, important explosion characteristics of gases and vapors, such as flammability limits, maximum explosion overpressure ( $P_{max}$ ), gas or vapor deflagration index ( $K_g$ ), and minimum oxygen concentration (MOC), can be determined with adherence to standardized test procedures.

#### 3.1. LEL and UEL for Gas and Solvent Vapors (Quiescent State)

By definition (ASTM, 1991), the lower explosion limit, LEL, of a gas/vapor is the highest concentration at which a gas/vapor explosion is not detected in three successive tests. For investigations under quiescent conditions, ignition energy (IE) is 10 J and

ignition delay time ( $t_v$ ) is 0 sec. The admixture of the OX /O<sub>2</sub>/ N<sub>2</sub> fuel directly takes place in the 20-L-Apparatus. Accordingly, the required OX /O<sub>2</sub>/ N<sub>2</sub> mixture can be produced readily with the partial pressure procedure.

In practice, the 20-L-Apparatus has to be cleaned thoroughly before each test. Then the test series starts with an initial gas sample concentration of 2 or 3 vol.%, followed by a stepwise decrease or increase of 0.25 vol.%. After the initial tests, these series are continued with a systematic increase of the gas concentration until ignition of the OX /O<sub>2</sub>/ N<sub>2</sub> mixture is observed. The test is then repeated with a gas concentration of 0.25 vol.% lower, and the concentration is reduced in further tests until no ignition of the OX /O<sub>2</sub>/ N<sub>2</sub> mixture is observed in at least three successive tests (Operating Instructions for the 20-L-Apparatus, 1996). The procedure for determining the UEL is similar to the procedure for determining the LEL.

Occasionally, estimating the flammability limits without experimental data may be necessary. Eqs. (1) and (2) are the ways to predict explosion limits of LEL and UEL for hydrocarbons. Since flammability limits are easily measured, experimental determination is always recommended (Jones, 1938; Crowl & Louvar, 1990).

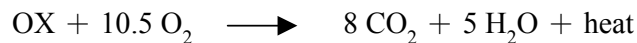
$$\text{LEL}=0.55 C_{\text{st}} \quad (1)$$

$$\text{UEL}=3.5 C_{\text{st}} \quad (2)$$

Where 0.55 and 3.5 are constants and  $C_{\text{st}}$  is the stoichiometric concentration which can be expressed as Eq. (3), is the volume % of fuel in fuel plus air.

$$C_{\text{st}} = (21/(0.21 + n)) \quad (3)$$

Where  $n$  is moles of O<sub>2</sub> required for the complete combustion of one mole of OX by the following reaction:



According to the above combustion reaction,  $n$  is 10.5 with the corresponding  $C_{\text{st}}$  of 1.96, so the LEL and UEL of OX at ambient pressure and temperature of theoretical values are 1.1 vol.% and 6.86 vol.%, respectively.

The coefficients of 21 and 0.21 in Eq. (3) are based upon the O<sub>2</sub> concentration in air. Therefore, by enhancing O<sub>2</sub> concentration, these two coefficients can be changed to higher values, such as 30 and 0.30; correspondingly higher LEL and UEL will be predicted by Eqs. (1) and (2). Therefore, by using Eqs. (1) and (2), theoretical values for the UEL and LEL of OX can be estimated. This estimate can save time by providing the

initial concentrations for the experiments to find the true value. However, the estimating method is only suitable for use at atmospheric pressure. If initial pressure is being enhanced, it should be by Eq. (5) as described below.

### 3.2. *Maximum Explosion Overpressure ( $P_{max}$ ), Maximum Rate of Explosion Pressure Rise $(dP/dt)_{max}$ , and Gas or Vapor Deflagration Index ( $K_g$ )*

The peak values that accompany the explosion of a combustible vapor are the maximum explosion overpressure ( $P_{max}$ ) and the maximum rate of explosion pressure rise  $(dP/dt)_{max}$ . Experimentally, the peak values can be obtained from tests over a wide range of concentrations using two chemical igniters (2×5 kJ) (Crowl & Louvar, 1990).

The explosion indices,  $P_{max}$  and  $(dP/dt)_{max}$ , are defined as the mean values of the maximum values of all three series. Subsequently, the gas or vapor deflagration index ( $K_g$ ) is calculated from  $(dP/dt)_{max}$  by means of the Cubic Law (NFPA, 1992)

$$V^{1/3} (dP / dt)_{max} = K_g \quad (4)$$

Where  $K_g$  and  $V$  are the maximum gas explosion constant specific to the gas and the volume of test apparatus (i.e., 0.02 m<sup>3</sup>), respectively.

As there are many gas products and industrial practices, it is appropriate to assign this maximum constant to one of several explosion classes (St), as shown in Table 2, and to use these as a basis for sizing explosive relief.

### 3.3. *Minimum Oxygen Concentration (MOC)*

The LEL is based on fuel in air. However, oxygen is the key ingredient, and an MOC is required to propagate a flame. When oxygen concentration is less than the MOC, the reaction cannot generate enough energy to heat the entire gas mixtures (including the inerts) to the extent required for the self-propagation of the flame. MOC is an especially useful parameter, because explosions and fires are preventable by reducing the oxygen concentration regardless of the concentration of the fuel. This concept is the basis for the common procedure called inerting (Crowl & Louvar, 1990; ASTM, 1991).

The MOC has units of per cent oxygen in air plus fuel. If experimental data are not available, the MOC is estimated by using the stoichiometry from the combustion reaction and the LEL. This procedure works quite well for many hydrocarbons (Siwek, 1996; Crowl & Louvar, 1990).

Below the MOC, an ignition of a specific mixture cannot occur in three

successive tests. In general, nitrogen is used as an inert gas; therefore, the following test conditions are based on nitrogen only.

After the first test series in normal air ( $O_2=21$  vol.%), the second series will be run at about 17 vol.%  $O_2$  in  $N_2$  over a wide range of gas concentrations, for determining the  $P_{max}$  and  $K_g$  explosion indices. Then the tests have to be continued by systematic reduction of the oxygen concentration in nitrogen until gas explosions are no longer possible.

### 3.4. Flammability Limit Dependence on Pressure

The initial pressure has little effect on the LEL except at very low pressure (<50 mmHg absolute), where flames do not propagate. The UEL increases significantly as the initial pressure is increased, broadening the flammability range. An empirical expression for the UEL for vapors as a function of pressure is available (Crowl, & Louvar, 1990).

$$UEL_p = UEL + 20.6(\log P + 1) \quad (5)$$

Where P is the pressure (mega pascals absolute) and UEL is the upper flammability limit (volume % of fuel at 760 mmHg).

However, the empirical expression for the UEL for vapors as a function of pressure is not available for all gases / vapors; nevertheless, an empirical expression can be found for the UEL specifically for OX by the regression of experimental data.

Vanderstraeten *et al.* (1997) correlated their data to an equation for the pressure dependence of the UEL (Eq. (6)) (Caron, *et al.* 1999).

$$UEL(P_1) = UEL(P_0) \left[ 1 + a \left( \frac{P_1}{P_0} - 1 \right) + b \left( \frac{P_1}{P_0} - 1 \right)^2 \right] \quad (6)$$

The OX experimental data are then used with Eq. (5), to estimate the UEL at the different initial pressures. If the error in UEL using Eq. (5) is significant, then coefficients a and b can be fed to Eq. (6). The prediction of UEL by the empirical expression of Eq. (6) is practically close to the real UEL of OX.

## 4. Results and Discussion

### 4.1. Explosion Classes (St)

The experimental results were the maximum explosion pressure from the

flammability limit tests versus various OX concentrations for the mixtures of OX /O<sub>2</sub>/ N<sub>2</sub>, with three initial pressures ( 760 mmHg, 1,520 mmHg, and 2,280 mmHg) at 150 °C as shown in Figs. 2, 3, and 4. Fig. 5 illustrates “UEL vs. O<sub>2</sub>” based on the experimental data obtained for the preceding figures. Fig. 5 shows that the UEL increases with increasing oxygen concentrations at the same initial pressure, and the UEL also increases with increasing initial pressure for the same initial oxygen concentration. Additionally, the MOC is shown to decrease with increased initial pressure.

Fig. 6 shows “P<sub>max</sub> vs. O<sub>2</sub>”, for the three initial pressures, 760 mmHg, 1,520 mmHg, and 2,280 mmHg, demonstrating the effect of oxygen concentration on the maximum pressure obtained from a stoichiometric OX /O<sub>2</sub>/ N<sub>2</sub> mix. A higher initial pressure results in a higher P<sub>max</sub>. This figure also indicates a dispersed and non-linear relationship between P<sub>max</sub> and the oxygen concentration.

In particular, the sensitivity of the K<sub>g</sub> and the P<sub>max</sub> to gas composition was examined. Stoichiometric mixtures of OX /O<sub>2</sub>/ N<sub>2</sub> were tested as a function of the oxygen concentration. For these tests, the gases were initially quiescent at a temperature of 150°C and one of three pressures prior to ignition. Fig. 7 illustrates that K<sub>g</sub> is highly dependent on initial pressure. Explosion class is also increased from St-0 to St-3, as calculated by Eq. (4).

In summary, all of the above values are shown in Table 3. The explosion overpressure is shown to significantly increase as oxygen concentration increases under the three initial pressures of 760 mmHg ~ 2,280 mmHg at 150°C.

#### 4.2. Flammability Diagram

Typically, the triangular flammability diagram can be used to represent all the possible mixtures of a three-component system. In practice, the use of triangular coordinates often makes examination of a three-component system easier because all three constants are presented on the graph at one time (Chad & Daniel, 1998; O’Shaughnessey & Power, 1995). The flammability diagram of an OX /O<sub>2</sub>/ N<sub>2</sub> mixture represents the three-components as X, O, N, respectively, and the areas encompassed by overlapping sets of oblique lines are the flammable zones for the three initial test pressures as shown in Fig. 8.

There are a number of models available in the literature that can be used to predict the pressure effect on flammable limits (O’Shaughnessey & Power, 1995). In general, the predictive models indicate that change in the lower flammable limit with increasing initial pressure would be minimal. However, the upper flammable limit rises dramatically, as shown in Fig. 8. Thus the vapor composition within the PA process reactor could well be located in the flammable zone under the reaction conditions.



In summary, the experimental results as shown in Fig. 8 depict the effects due to the changes in initial pressure. However, the flammable limits did not vary as conspicuously with an increasing initial pressure as was estimated from the models. This indicates the flammable composition region did not change with increasing initial pressure as dramatically as predicted. The corresponding explosion areas are 25%, 30% and 35% for 760 mmHg, 1,520 mmHg, and 2,280 mmHg, respectively, as shown in Fig. 8. The deviation from the limits proposed by the predictive models is most likely due to the physical nature of the OX, in the vapor. To ensure that all of the OX used in the experiments is in the vapor state, all experiments must be controlled to exceed the boiling point of OX (144°C).

A point called Out of Service Fuel Concentration (OSFC) (Chad & Daniel, 1998; O'Shaughnessey & Power, 1995) is utilized to avoid entering the flammability zone when air is introduced to the vessel containing 100 % fuel. Similarly, a point called In Service Oxygen Concentration (ISOC) (Chad & Daniel, 1998; O'Shaughnessey & Power, 1995) is applied to keep oxygen concentration below MOC while fuel is introduced into to the vessel.

The OSFC and ISOC are calculated by Eqs. (7) and (8) (Chad & Daniel, 1998).

$$OSFC_{MOC} = \frac{MOC}{Z \left( 1 - \frac{MOC}{21} \right)} \quad (7)$$

$$ISOC_{MOC} = \frac{MOC \times Z}{\left( Z - \frac{MOC}{100} \right)} \quad (8)$$

From the experimental result, the MOC of OX is 10 vol.% under the initial temperature of 150°C and the initial pressure for 2,280 mmHg. As far as safety is concerned, it is considered to be the most conservative approach under OX experimental condition, but from the combustion equation of OX, the Z is 10.5. Therefore, the OSFC and ISOC are calculated to be 1.8 vol.% 10.1 vol.%, respectively, and are illustrated as shown in Fig. 8.

The oxygen operating concentration of 21 vol.% to 40 vol.% is established for this study. However, at 2,280 mmHg, the experiment can only be conducted with oxygen of 21 vol.%, simply because the pressure sensor cannot read over 25 bara and the maximum tested pressure of 20-L-Apparatus is 39 bara. A hazardous situation is likely if the maximum tolerance value of the 20-L-Apparatus is exceeded.

The application of the expanded flammable limits was significant. As expected, the decrease of MOC was insignificant (as shown in Figs. 2, 3 and 4). Increasing the initial pressure generally expands the flammable limits, but as shown in Fig. 8, the expansion is smaller than anticipated, especially with a hydrocarbon as the fuel.

Therefore, changing from 760 mmHg to 2,280 mmHg had a less than expected influence on the expansion in the flammable limits of OX. This is most likely due to the physical structure of the OX, causing the slight change of vaporization under various pressures.

#### 4.3. *Simulating Equation of UEL for OX with Respect to Different Initial Pressures*

With initial pressures, the experimental results, which are calculated from Eq. (5), show that the predictive UEL of 1,520 mmHg, and 2,280 mmHg are, respectively, 11.6 vol.%, and 15.2 vol.%. The experimental results, however, are respectively 6.4 vol.%, and 8.0 vol.%; hence Eq. (6) should be used to model the experimental data, and curve fitting the experimental data must be used to find the correlation constants. The equation using these constants is only valid in the pressure range between 760 mmHg and 2,280 mmHg. The values of the calculated coefficients a and b are 0.13 and 0.06, respectively.

By inserting the values of coefficients a and b, Eq. (6) can be modified to Eq. (9) which can, in turn, predict the UEL at the initial pressure (1.2 bara to 1.45 bara) of the OX process to be 5.6 vol.% to 5.8 vol.%.

$$UEL(P_1) = UEL(P_0) \left[ 1 + 0.13 \left( \frac{P_1}{P_0} - 1 \right) + 0.06 \left( \frac{P_1}{P_0} - 1 \right)^2 \right] \quad (9)$$

The estimated composition in the vapor space of a plant reactor is well above the upper explosion limit for the mixture during the course of the reaction under the specified reaction conditions (as shown in Fig. 8). The estimation equation has shown a very close approximation to the vapor composition of OX being analyzed at the end of the reaction. Therefore, the assumption that was made in calculating vapor compositions is reasonable and valid. In practice, further calculations could be used to estimate the operating vapor composition lines at higher and lower temperatures and pressures. In general, some specific equations could probably be found for various chemicals with combustible nature to predict their process flammability zone. In summary, the specific process temperature and pressure under which a vapor mixture is likely to become flammable can be determined.

## 5. Conclusions and Recommendations

By enhancing O<sub>2</sub> to 40 vol.% in a OX /O<sub>2</sub>/ N<sub>2</sub> mixture, the testing results demonstrated that the OX explosion class changes from St-0 to St-3, showing an increased degree of hazard. Furthermore, MOC is an important safety property in that explosions will never occur below the MOC. However, providing a safety margin is recommended. MOC will be decreased with increasing initial pressure. This indicates that O<sub>2</sub> concentration is a crucial factor for assessing fire and explosion hazards (Lees, 1991; Shu, *et al.* 2000).

Increasing initial pressure will increase PA yield from process conditions, but it could also widen the flammable zone so that the degree of hazard becomes greater. Therefore, preventing PA process conditions from falling into the flammable zone at higher pressure is vital. The vapor compositions under expected normal plant operating conditions are well above the experimental upper flammable limit, and hence, the atmosphere will be nonflammable during the reaction period.

The process operating conditions, to avoid formation of flammable mixtures, should be controlled such that the flammable region is never entered. This can be done by charging materials to the reactor under ambient conditions, as no flammable mixtures will form under these conditions. By purging with nitrogen, the sealed reactor can be kept under lower oxygen content than the MOC. Temperature and pressure trips can initiate the injection of nitrogen as the reactor is heated to reaction temperature if process deviations occur.

Thus, the process can be operated safely above the upper explosion limit with appropriate shut down procedures that respond to temperature and pressure deviations that could drive the vapor composition near the flammable region.

Using a 1-L-Apparatus, as shown in Fig. 9, is recommended for future study to compare OX data with data from the 20-L-Apparatus run under the same pressure and temperature. Characteristics of the 1-L-Apparatus are that the maximum test pressure is 224 bara and the maximum temperature is 400°C. Then the OX flammability zones for various operating conditions can be analyzed and compared. Meanwhile, by using the equations, valuable and relevant information can be acquired from both the 20-L-Apparatus and the 1-L-Apparatus.

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## 7. References

- ASTM (1991). Standard test method for concentration limits of flammability of chemicals E 681-85. Philadelphia, PA, USA: American Society for Testing and Materials.
- ASTM (1993). Standard practice for determining limits of flammability of chemicals at elevated temperature and pressure E 981-83. Philadelphia, PA, USA: American Society for Testing and Materials.
- Caron, M., *et al.* (1999). Pressure dependence of the auto-ignition temperature of methane/air mixtures. *Journal of Hazardous Materials*, A65, 233-244.
- Chad, V.M. & Daniel, A.C. (1998). Application of the flammability diagram for evaluation of fire and explosion hazard of flammable vapors. *Process Safety Progress*, 17(3), 176-183.
- Chem. Systems Inc., (1995), (pp. 10-17). Menlo Park, California, USA.
- Crowl, D.A. & Louvar, J. F. (1990). *Chemical process safety: fundamentals with applications* (pp. 157-192). New Jersey, USA.
- Davies, R. (1979). Air oxidation process hazards--an overview. *Journal of Loss Prevention in the Process Industries*, 12, 103-110.
- Graham, J. J. (1970). The fluidized bed phthalic anhydride process. *Chemical Engineering Progress*, 66(9), 54-58.
- Jones, G. W. (1938). Inflammation limits and their practical application in hazardous industrial operations. *Chemical Review*, 22(1), 1-26.
- Lees, F. P. (1991). *Loss Prevention in the Process Industries*, Vol. 2, 2nd edn. (pp. 140-172). Butterworth-Heinemann, UK.
- Lewis, R. J., (1996). *SAX'S dangerous properties of industrial materials*. Van Nostrand Reinhold, Vol. 3-4, 9th edn. (pp. 3404). New York, USA.
- NFPA (1992). *Guide for venting of deflagrations*. National Fire Protection Association NFPA 68. Quincy, MA, USA.
- Operating Instructions for the 20-L-Apparatus (1996), (pp. 6-66). Kühner, Birsfelden, Switzerland.
- O'Shaughnessey, D. & Power, B. (1995). Simulating flammability under process conditions. *Process Safety Progress*, 14(1), 22-25.
- Park, C. M. & Sheehan, R. J. (1996). Phthalocyanine compounds. *In Kirk-Othmer (Ed.) Encyclopedia of Chemical Technology*, Vol. 18, 4th edn. (pp. 991-1043). New York, USA.
- Petroleum Chemicals of ROC & Petroleum Chemical Labor Union of Taiwan, 2001.

- Schwab, R.F., (1991). Dust explosion. In McKetta, J. J. & William, A. C. (Ed.) *Encyclopedia of Chemical Processing and Design*, Vol. 17 (pp. 67-96). New York, USA.
- Schwab, R. F. & Doyle, W. H. (1970). Hazards in phthalic anhydride plants. *Chemical Engineering Progress*, 66(9), 49-53.
- Siwek, R. (1996). Determination of technical safety indices and factors influencing hazard evaluation of dusts. *Journal of Loss Prevention in the Process Industries*, 9(1), 21-31.
- Shu, C.M., et al. (2000). Determination flammability area of o-Xylene at high temperature. *Ottawa, Canada: Conference of North American Thermal Analysis Symposium*.
- Vanderstraeten, B. et al. (1997). Experimental study of the pressure and temperature dependence on the upper flammability limit of methane/air mixture. *Journal of Hazardous Materials*, 56, 237-246.

## 8. Nomenclature

- a : Coefficient of Eq. (6)
- b : Coefficient of Eq. (6)
- $C_{st}$  : Stoichiometric concentration (vol.%)
- IE : Ignition Energy (J)
- ISOC : In Service Oxygen Concentration (vol.%)
- $K_g$  : Gas or vapor deflagration index ( $m \cdot \text{bara}/\text{sec}$ )
- LEL : Lower Explosion Limit (vol.%)
- MOC : Minimum Oxygen Concentration (vol.%)
- OSFC : Out of Service Fuel Concentration (vol.%)
- P : Pressure (bara)
- $P_0$  : Initial pressure (bara)
- $P_1$  : Dispersion pressure (bara)
- $P_{max}$  : Maximum explosion pressure (bara)
- $(dP/dt)_{max}$  : Maximum rate of pressure rise with time (bara/sec)
- $t_v$  : Ignition delay time (sec)
- UEL : Upper Explosion Limit (vol.%)
- V : Volume ( $m^3$ )
- PH : Higher Pressure (bar)
- PL : Lower Pressure (psi)

Table 1

Phthalic anhydride capacity and expansion projects in Taiwan.

(unit : thousand tons)

Product	Company	Capacity before year 2001	Expansion after year 2001
Phthalic Anhydride (PA)	Nan Ya Plastics Corporation	100	100
	Union Petro Chemical Corporation in Taiwan	60	90
	Union Petro Chemical Corporation in China	0	50
	Cracker No.7 (Expected)	0	120
	Taiwan Oil Product Corporation	60	130

Data from (Petroleum Chemicals of ROC & Petroleum Chemical Labor Union of Taiwan, 2001).

Table 2

Relation between  $K_g$  and explosion classes (St), (NFPA, 1992).

$K_g$ (bar-m/sec)	Explosion Classes (St)
<1	St-0
1 - 200	St-1
201 - 300	St-2
> 300	St-3

Table 3

Fire and explosion characteristics of OX at 150°C with three initial pressures 760 mmHg, 1,520 mmHg, 2,280 mmHg, respectively.

O <sub>2</sub> (vol.%)	LEL (vol.%)	UEL (vol.%)	P <sub>max</sub> (bara)	(dP/dt) <sub>max</sub> (bara · sec <sup>-1</sup> )	K <sub>g</sub> (m · bara · sec <sup>-1</sup> )	Explosion Class (St)
<b>150°C/760 mmHg</b>						
12	0	0	0	0	0	St-0
13	0.875	2	1.5	2	0.54	St-0
15	0.875	2.75	4.2	45	12.21	St-1
17	0.875	3.75	2.7	164	44.5	St-1
21	0.875	5.375	5.9	403.33	109.5	St-1
30	0.875	8.125	8.1	1,441	391	St-3
40	0.875	13.125	10.1	2,906	788.8	St-3
<b>150°C/1,520 mmHg</b>						
11	0	0	0	0	0	St-0
12	0.625	2	0.4	2	0.54	St-0
13	0.625	3	5.2	5	1.35	St-1
17	0.625	4.5	10.5	192	51.84	St-1
21	0.625	6.375	13.6	817	221.8	St-2
30	0.625	10.5	17.9	2,960	803.47	St-3
40	0.625	15.5	22.9	7,250	1,967.9	St-3
<b>150°C/2,280 mmHg</b>						
10	0	0	0	0	0	St-0
11	0.5	3	0.5	6	1.62	St-1
13	0.5	4	8.1	6	1.62	St-1
17	0.5	5	17	339	91.53	St-1
21	0.5	8	23	1,883	508.41	St-3

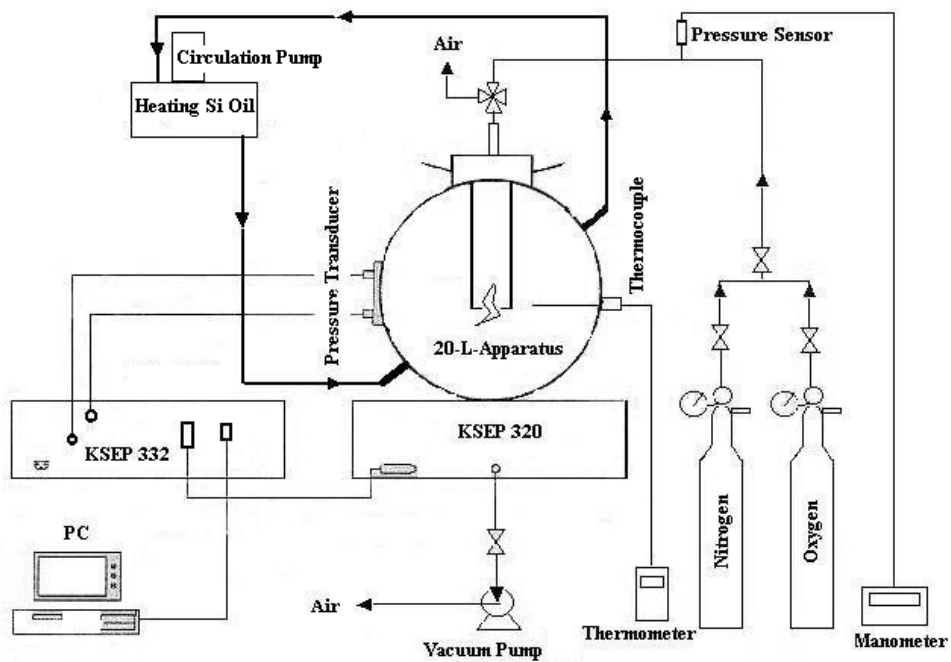


Fig. 1. A schematic diagram of the 20-L-Apparatus control system diagram.



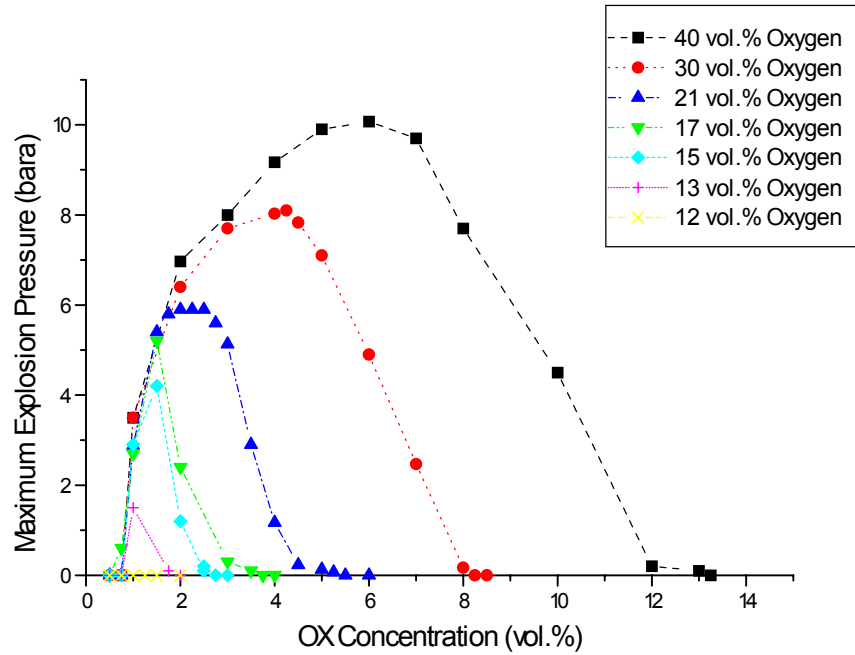


Fig. 2. Maximum explosion pressure vs. OX concentration at 150°C/760 mmHg.

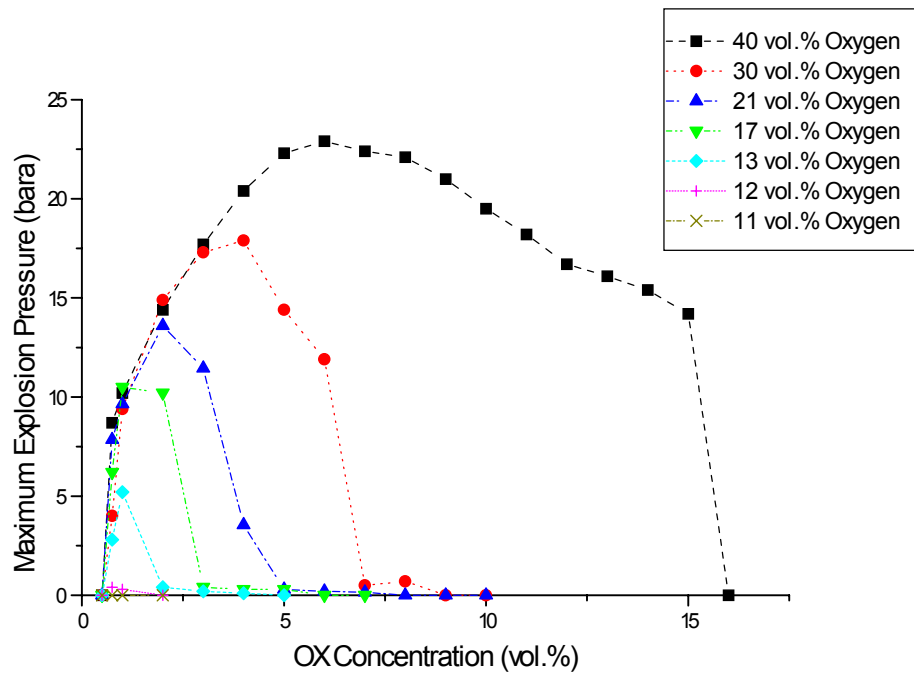


Fig. 3. Maximum explosion pressure vs. OX concentration at 150°C/1,520 mmHg.

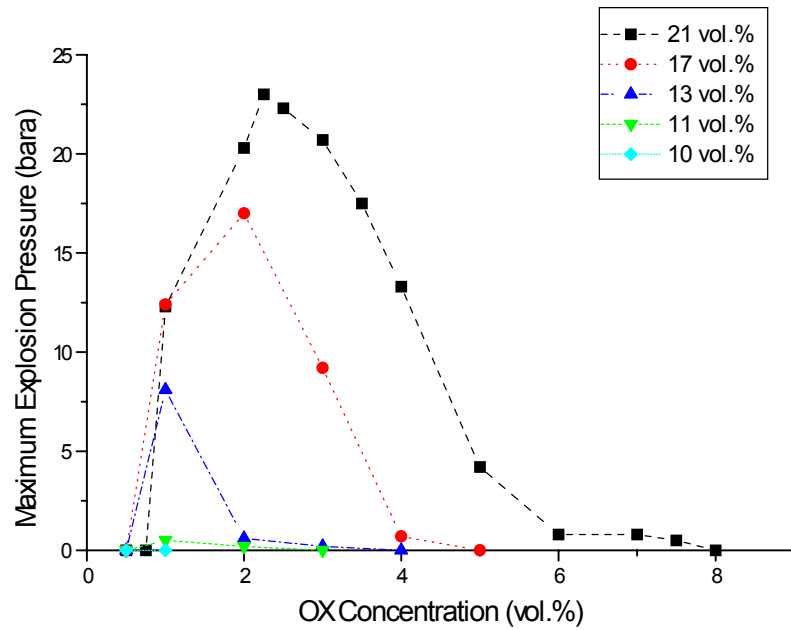


Fig. 4. Maximum explosion pressure vs. OX concentration at 150°C/2,280 mmHg.

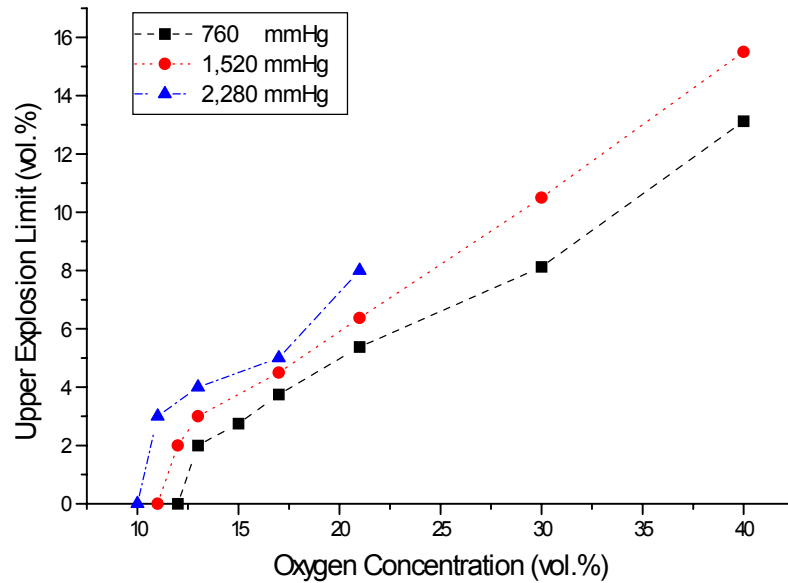


Fig. 5. Upper explosion limit vs. oxygen concentration with OX at 150°C and three different initial pressures.

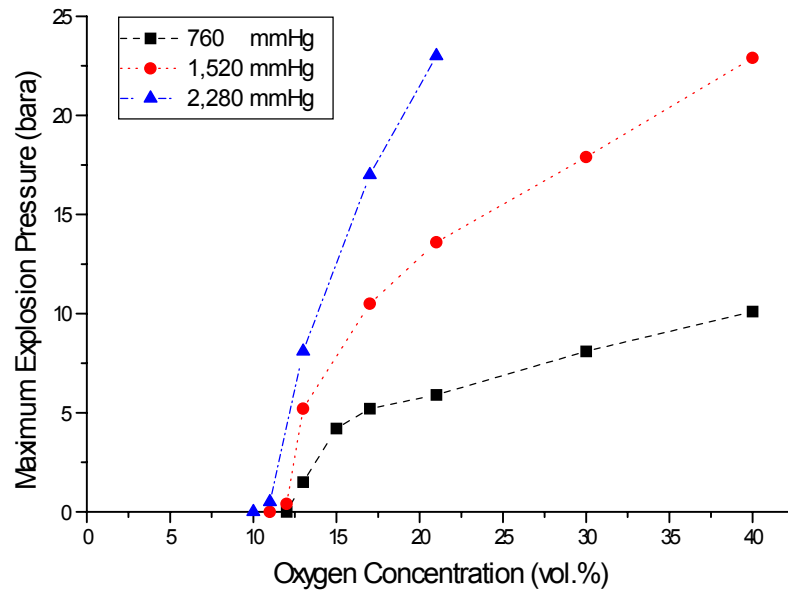


Fig. 6. Maximum explosion pressure vs. oxygen concentration with OX at 150°C and three different initial pressures.

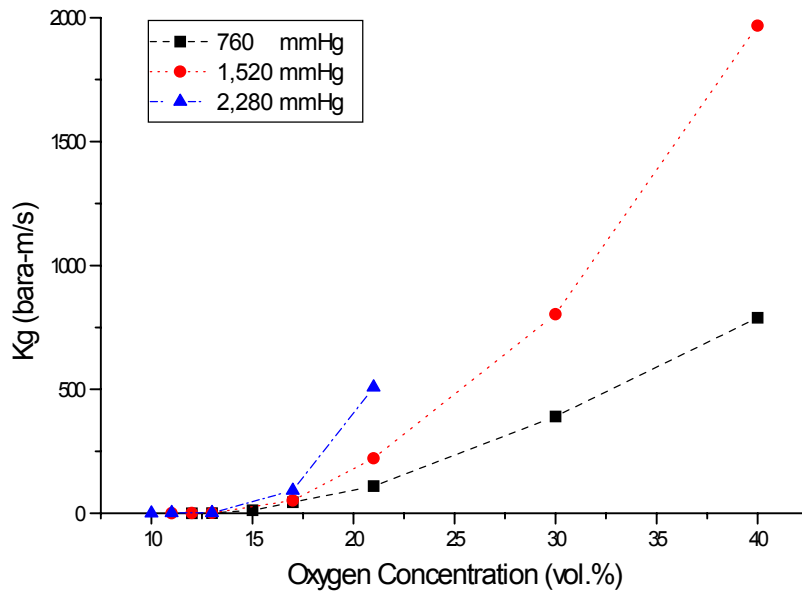


Fig. 7.  $K_g$  vs. oxygen concentration with OX at 150°C and three different initial pressures.

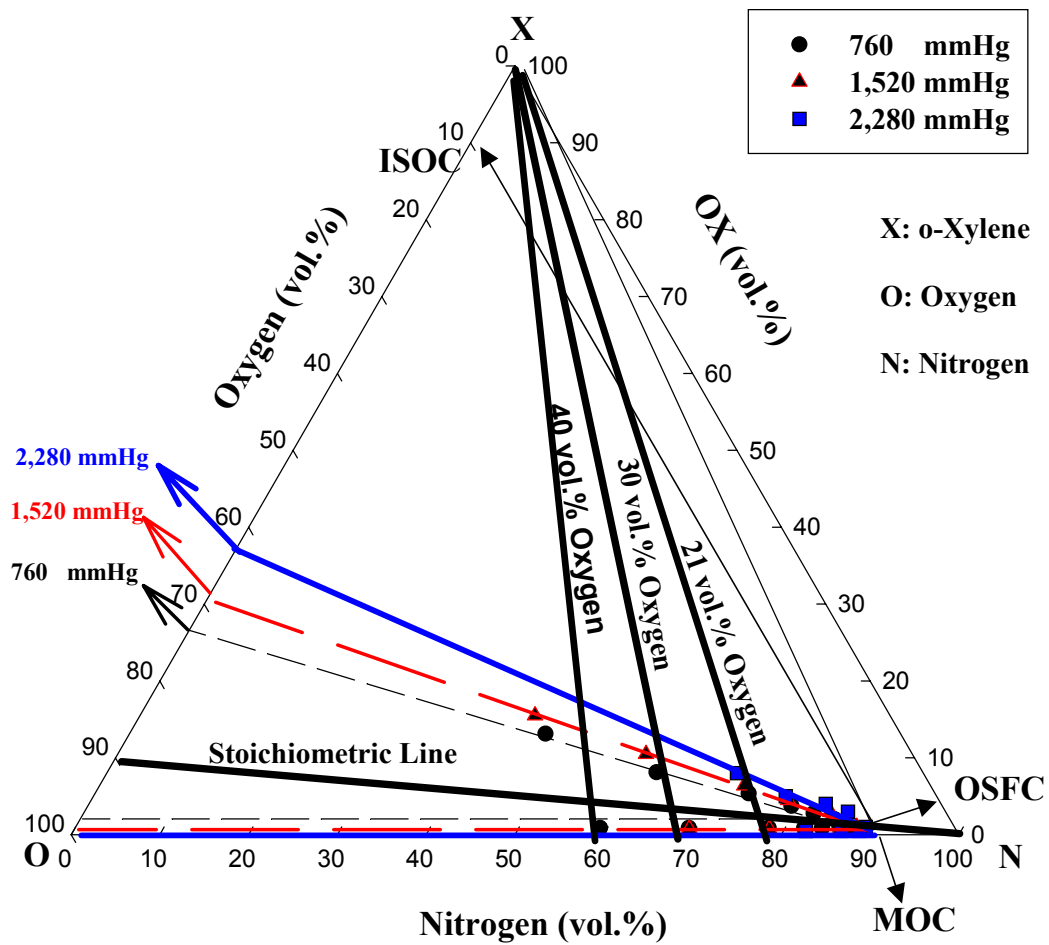


Fig. 8. Overall triangular flammability diagram illustrating contrasting the change in flammability zone with increased of initial pressure.

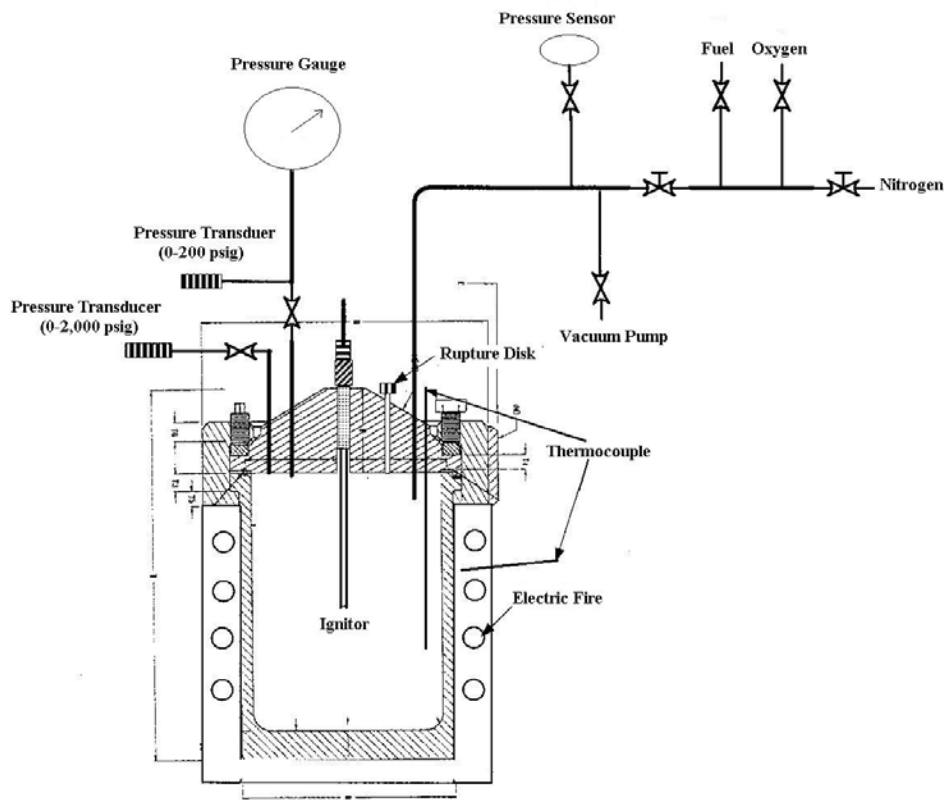


Fig. 9. A schematic diagram of the 1-L-Apparatus and its control system (ASTM, 1993).